KINETICS OF OXIDATION OF SODIUM DITHIONITE

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In Partial Fulfilment of the Requirements
for the degree of
DOCTOR OF PHILOSOPHY

By
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CERTIFICATE

Certified that the work 'KINETICS OF OXIDATION OF SODIUM DITHIONITE' has been carried out under our supervision and that the work has not been submitted elsewhere for a degree.

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D.K. Singh
Author

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NOMENCLATURE

[I]	inhibitor concentration, moles/liter
k_i, k_2, etc	rate constants for reaction steps
M	concentration, moles/liter
$[O_2]$	average oxygen concentration
r	rates, moles/(liter)(second), $-\frac{d[O_2]}{dt}$
$[S_2O_4^{=}]$	average dithionite concentration
t	times, sec
T	absolute temperature ^{o}K
$\underset{\cdot}{SO}_2^-, \underset{\cdot}{OH}, \underset{\cdot}{SO}_4^-$	free radicals

RUNS

RP	effect of pH: uninhibited runs
RO	effect of Oxygen: unhibited runs
RD	effect of dithionite: unhibited runs
RT	effect of temperature: uninhibited runs
CI	effect of $MnCl_2$: inhibition with $MnCl_2$
OI	effect of Oxygen: inhibition with $MnCl_2$
DI	effect of dithionite: inhibition with $MnCl_2$
SI	effect of $MnSO_4$: inhibition with $MnSO_4$
OS	effect of oxygen: inhibition with $MnSO_4$
DS	effect of dithionite: inhibition with $MnSO_4$
TI	effect of triethanolamine: inhibition with triethanolamine
OT	effect of Oxygen: inhibition with triethanolamine
DT	effect of dithionite: inhibition with triethanolami

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SYNOPSIS

The kinetics of the reaction of oxygen with sodium dithionite in aqueous solutions have been studied by a flow thermal method of HARTRIDGE and ROUGHTON. This method eliminates the effects of diffusion, and provides a technique for measurements in fast homogeneous reactions. The oxidation was studied in wide ranges of temperature, pH and reactant concentrations. Experiments were also conducted to study the inhibition of this reaction.

Results on the oxidation study of dithionite solutions at $30^{\circ}C$ show that the reaction is first order with respect to dithionite and zero order with respect to oxygen. An activation energy of 17.5 Kcal/g-mole has been calculated for this reaction.

The inhibiting effects of manganese chloride, manganese sulfate and triethanolamine have been studied at 30^{o}C. An identical behaviour in the inhibiting effects of $MnCl_2$ and $MnSO_4$ was observed. In these cases, the rate was inversely proportional to approximately one power of the total concentration of manganese added to the reacting solution. The effect of triethanolamine was inversely proportional to 0.2 power of the total concentration of triethanolamine. In all cases the reaction was found to be first order in dithionite and zero order in oxygen.

A free radical chain mechanism has been proposed and the rate expressions derived satisfactorily account for the kinetics of the dithionite oxidation with and without inhibitior The inhibition step is believed to follow a different termination path.

Parametric dependence of pH of the reacting medium on the reaction rate has also been followed. It has been observed that the rate decreases in a regular pattern with increase of pH. This has been attributed to the possibility of dithionite undergoing hydrolysis as a result of which the available dithionite concentration for oxidation is reduced.

It is expected that the present study would contribute to the understanding of kinetics and mechanism of this reaction

CHAPTER 1

INTRODUCTION

1.1 General

Solutions of sodium dithionite are used as powerful and rapid reducing agents for vat dyeing, bleaching and for manufacture of various chemicals. The inherent instability of this compound with respect to atmospheric oxidation in aqueous solutions, however, lowers the efficiency of the solutions after prolonged storage. A considerable excess of sodium dithionite over stoichiometric amounts has, therefore, to be used. As an industrial practice it would be very much desirable to minimise the excess consumption of sodium dithionite. It is essentially in regard to this problem that the kinetics of sodium dithionite oxidation in aqueous solutions has been studied in some details. The resulting information, however, is contradictory in many ways and therefore remains inconclusive.

1.2 Literature Review

The earliest air oxidation study was conducted by Meyer [1]. He studied the oxidation of sodium dithionite by observing the oxygen uptake in shaken flasks containing aqueous sodium dithionite solution. The results showed that the products of reaction were sulfite and sulfate. A primary reaction was proposed as

$$H_2S_2O_4 + H_2O + O_2 = H_2SO_4 + H_2SO_3 \qquad (1.1)$$

Also, a competing reaction was described as

$$2H_2S_2O_4 + 2H_2O + O_2 = 4H_2SO_3 \qquad (1.2)$$

From overall reaction rates the author computed first order rate constants but found that they drifted over a wide range.

Basset and Durrant [2] studied the reaction between dithionite and molecular oxygen. According to them the oxidation mechanism was based on the arguments that the dithionite exists in three isomeric forms. Each isomer was believed to decompose in a way that all of the reaction products could be explained by one or more of the mechanisms. Although Basset and Durrant's work is of considerable value as an compilation of experimental observations of dithionite reaction, subsequent work has invalidated their interpretations.

Nicloux [3] determined the overall stoichiometry of the reaction between dithionite and oxidising agent of varying strengths. Comparatively weak oxidizing agents such as silver ion, oxidized sodium dithionite to sodium sulfite. With molecular oxygen, an equimolar mixture of sulfite and sulfate was formed. Finally with very strong oxidizing agent sulfate was the only product. Nicloux [3] established that aqueous solutions of $Na_2S_2O_4$ react with oxygen according to the stoichiometry:

$$Na_2S_2O_4 + O_2 + H_2O = NaHSO_4 + NaHSO_3 \quad (1.3)$$

No experimental details were given.

Lynn [4] tried to get more experimental data on the rate of atmospheric oxidation of sodium dithionite with the objective of finding the conditions under which the rate of these reactions is reduced. The measurements were made at 50°, 60° and 70°C. The effect of NaOH additive in the solutions on the rates of reaction was also measured. The reactions appeared to be sufficiently complicated and no kinetic mechanism was ascertained for inhibition of this reaction. He suggested that the atmospheric oxidation of dithionite proceeded, according to first order mechanism with respect to dithionite and that rate increased with temperature. He stated that the overall stoichiometry was described by the reaction (1.3).

An examination of his data at 50°C showed that the oxidation rate increased with increase in air flow which meant that the diffusion rate of oxygen was contributing factor. Without correcting for diffusion his results for actual oxygen-dithionite reaction were, therefore, only approximate. His experiments also showed that in presence of 0.1 M sodium hydroxide the rate was inhibited and the reaction proceeded smoothly.

Rinker et al. [5] conducted a study of air oxidation of sodium dithionite in aqueous solution which was 0.1 M in

sodium hydroxide. The concentration of dithionite was measured as a function of time at 30°, 40°, 50° and 60°C. Under conditions in which diffusion of air was not controlling, it was found that the oxidation was half order with respect to dithionite and first order with respect to molecular oxygen. A free radical chain mechanism for dithionite oxidation, as given below, was proposed.

$$
\begin{aligned}
&S_2O_4^{--} \rightleftharpoons 2\underset{\cdot}{S}O_2^{-} \\
&\underset{\cdot}{S}O_2^{-} + O_2 \rightleftharpoons \text{Complex B} \xrightarrow{k_2} SO_2 + \underset{\cdot}{O}_2^{-} \\
&\underset{\cdot}{S}O_2^{-} + \underset{\cdot}{O}_2^{-} \xrightarrow{k_3} SO_2 + \underset{\cdot}{O}_2^{--} \\
&\underset{\cdot}{O}_2^{--} + H_2O \xrightarrow{k_4} \underset{\cdot}{H}O_2^{-} + \underset{\cdot}{O}H^{-} \\
&\underset{\cdot}{H}O_2^{-} + \underset{\cdot}{S}O_2^{-} \xrightarrow{k_5} \underset{\cdot}{S}O_4^{-} + \underset{\cdot}{O}H^{-} \\
&\underset{\cdot}{H}O_2^{-} + \underset{\cdot}{S}O_2^{-} \xrightarrow{k_6} \underset{\cdot}{S}O_2^{--} + \underset{\cdot}{O}H \\
&\underset{\cdot}{O}H + \underset{\cdot}{S}O_2^{-} \xrightarrow{k_7} SO_2 + \underset{\cdot}{O}H^{-} \\
&SO_2 + OH^{-} \xrightarrow{k_8} SO_3^{--} + H^{+} \\
&\tfrac{1}{2}SO_3^{--} + \tfrac{1}{4}O_2 \xrightarrow{k_9} \tfrac{1}{2}SO_4^{--}
\end{aligned}
$$

These authors, however, did not give any rate expression to satisfy their kinetic data.

Morello et al. [6] studied the rate of removal of O_2 from aqueous solution by sodium dithionite in 0.1 M sodium hydroxide in a rapid reaction apparatus, using a membrane covered polarographic cell to determine partial pressure of oxygen in the flowing liquid. The measurements

were made at 37°C so that their data could be applicable in studies of the kinetics of oxyhaemoglobin in blood. The initial concentrations in the mixed reacting solutions were between 8 x 10^{-5}M and 47.5 x 10^{-5}M for dithionite and either 10 x 10^{-5}M or 47.8 x 10^{-5}M for O_2. The reaction over the first 40 msec was found to be first order with respect to dithionite and zero order with respect to molecula oxygen. The initial rate constant was 42.5 ± 3.6 sec^{-1}.

Jhaveri and Sharma [7] used a jet apparatus to study the kinetics of absorption of oxygen in aqueous solutions of sodium dithionite. The reaction was found to be first order with respect to dithionite concentration below 0.08 M and second order with respect to dithionite above 0.08 M. The reaction was also studied by them in a stirred cell and a small laboratory packed column, wherein it was found to be zero order with respect to oxygen for all dithionite concentrations. They also investigated the effect of NaOH concentration on the reaction rate.

It has been claimed that variety of substances, as described below, could be used to retard the rate of this reaction.

Mecco [8] suggested that at high temperature for vat dyeing the consumption of sodium dithionite is greatly increased. Addition of 0.01 to 1 per cent of a trialkanolamine (based on the amount of dithionite) to the vat dyeing

bath decreases the consumption of hydrosulphite and improves the dyeing. Thus a bath containing NaOH, $NaClO_3$, and triethanolamine was heated to approximately 200°F and $Na_2S_2O_4$ was added. The rate of dithionite consumption was approximately 0.11 oz/gal/min as measured by titration with a standard indigo solution. The consumption rate was twice as great as in a corresponding bath containing no triethanolamin Manganese compounds, such as $MnCl_2$, $MnSO_4$ and Mn-resinate, can be used to inhibit this oxidation reaction.

Klemin [9] found that triethanolamine is the best stabilizing agent as compared to NaOH, Na_2CO_3, ethanol, pyridine, ethylene glycol and glycerol.

It has also been suggested that sodium phosphate, syrum sodium silicate, pyrogallic acid, ammonium thiocynate and chloroform could be used to inhibit the rate of oxidation of dithionite[38].

All of the investigators employed alkaline reaction medium since in acidic medium the reaction rates were observe to be extremely high to make meaningful measurements. Althou the quantitative effect of pH on the oxidation rate has not been studied still an implication of this observation is that an increase in pH of the reacting medium tends to slow down the reaction.

The kinetic analysis to establish reaction mechanism has not been projected as a focal point obviously because of

existing controversy in experimental results. As noted above that some substances are known to inhibit the oxidation of sodium dithionite solutions, yet there seems to be no reported data on kinetics and inhibition. This indicates the need for a study of existing techniques and the undertaking of an experimental study of this system with the object of obtaining rate data and establishing a reaction mechanism.

1.3 Measurement of Fast Reaction Rates

In measurement of reaction rates in chemical kinetics the rates can vary from zero to very large values, and it is influenced by a large number of variables which describe the condition of the reacting system. Temperature, pressure, composition of reaction mixture, presence or absence of a catalyst/inhibitor - all of these may have an important effect on the reaction rate.

Elimination or separation of diffusion effects from kinetic effects is the major problem determining the true kinetic reaction rate constant, while the rates of fast homogeneous reactions are measured in solution.

Following are the methods published in the literature for measuring the rates of fast homogeneous reactions in solution.

1.3.1 Electrochemical Method

The rate of a chemical reaction is measured in competition with rate of diffusion. The concentration at the surface is changed by the electrochemical method and the species are then formed by diffusion and chemical reaction in this reaction layer at the electrode surface.

Delahey [10] has measured the potential-time transient at constant current at a mercury electrode. Various theoretical and experimental methods for the determination of the rate constants of the kinetic processes are presented. Only the first order processes can be interpreted rigorously because theoretical analysis of the reactions of a higher order require the solution of non-linear differential equations: the mathematical treatment then involves approximate methods.

Polarographic measurement studies were made by Levine et al. [11] and Yagi and Inoue [12]. The system used was oxygen sulfite ion in the liquid phase. The application of polarography with the dropping mercury electrode is limited in the anodic range of potentials by the oxidation of mercury. Kinetic and catalytic processes can only be studied semi-quantitatively by this method because of the complexity of hydrodynamic problem.

1.3.2 Magnetic Resonance Method

Proton magnetic resonance in pure liquid ammonia, and in solutions of water, KNH_2, $NaNH_2$, NH_4Br and N_3HBF_3 in this solvent was studied by Ogg [13]. It is a semi - quantitative method. Only extremely fast or ultra-rapid reactions could be studied. This method is not applicable for high activation energy reactions.

1.3.3 High Frequency Method

Elving [14] has shown the application of high frequency oscillators to the measurements of rapid reaction. The author has described in detail the measurements of the rate of alkaline hydrolysis of esters. The high frequency technique has an inherrent limitation in that only one physical property such as conductance, refractive index or volume can be measured. The interpretation of this method are apparently more complex. For aqueous solutions, the applicability of the high frequency technique is limited to concentration equivalent to 10^{-1} to 10^{-3} M in electrolyte i.e. quite dilute solutions.

1.3.4 Radioactive Tracers

Radioactive tracer technique has been used by Himmelblau and Babb [15] to determine the kinetic reaction rate constants in the CO_2-$NaHCO_3$-Na_2CO_3-H_2O system at temperatures of 32°, 50° and 68°F. Earlier work related

to this technique has been described by Mills and Urey [16]. The essence of the procedure is to operate the system at chemical equilibrium and isotopic disequilibrium. The method is reliable and has applications in the field of heterogeneous reactions. A specialised laboratory is required for this technique because of its complexity.

1.3.5 Flow Techniques:

Hartridge and Roughton [17] have done the pioneering work on flow techniques. Their technique with modifications has been applied to reactions with half times from ten seconds to 0.001 second . The two solutions which are to react are placed in containers and driven thence into a mixing chamber; the emerging mixed fluid then passes down an observation tube and at various cross sections the composition of flowing solution is determined by optical, thermal, chemical, electrical or other methods of analysis applicable to rapidly moving fluids. With a knowledge of flow velocity of the solution in the observation tube and of the position of observation, the amount of reaction can be related to the amount of elapsed time since the two reactants were mixed.

Roughton, Chance, Page and others [18-28] have described various applications of rapid mixing techniques. In all of the flow methods, mixing chamber requires a careful attention for optimum conditions.

Following are the various measuring techniques employed in the flow method.

1.3.5.1 Photo Electric Method

Dalziel [27] has described the use of the modern spectrophotometer with the constant flow method. The design and scope of the apparatus have been described by Millikan [18]. This method is applicable to reactions in which a reactant or product absorbs visible or ultravoilet light, while the other components do not. Caldin and Trowse [28] have described an apparatus for measuring the rates of fast reactions involving color changes in solution. The operation is semiautomatic and gives a complete photographic record, thus avoiding personal error.

1.3.5.2 Quenching Methods

Pinsent [29] has described the application of conventional quenching methods to a Hartridge-Roughton type flow apparatus for reactions with half-times in the range 50 m sec to 2 sec. Frost and Pearson [30] have described the fluorescence quenching.

The results given by this method are reproducible to ± 7 per cent for a reaction with a half-time of 50msec to 2 sec.

1.3.5.3 Thermal Methods

The principle of thermal method consists simply in

measuring (by thermoelectric or other methods) the temperature of mixed fluid at different cross-sections of the observation tube, and calculating from these measurements the amount of heat evolved and thence the amount of chemical change which has occurred [31].

Roughton [32] has extended the method of Hartridge and Roughton [31] to the measurement of the amount of heat liberated in rapid reactions, within periods of 10msec or less from the commencement of such reaction. Roughton has carried out extensive tests of the physical sources of error involved in the measurement of thermo junctions of temperature of rapid moving fluids. The above method is also useful for slow reactions. Bateman and Roughton [33] further improved the apparatus by improved thermal control which enabled them to follow to within 1-2 per cent the time course of heat effects over a period of 0 to 10 msec even when the total temperature change was no greater than 0.01^{o}C. Roughton [34] applied the technique of Bateman and Roughton to the study of kinetics of formation of carbon dioxide from bicarbonate with acid.

Pearson et al. [35] have further developed the flow calorimeters of Bateman and Roughton. It is a constant flow type, where a stationary state of reaction establishes itself at any point in the observation tube. They used a galvanometer of much shorter period than that used by Bateman

and Roughton and a recording system which shortened the response time of the temperature sensing system.

Pinsent, Pearson and Roughton [36, 37] used the technique developed by Pearson, Pinsent and Roughton [35]. The above authors studied the kinetics of combination of carbon dioxide with ammonia. The published data are considerably more extensive than any hitherto available.

Except for Hartridge and Roughton's method, the methods described are seldom used. Most of them have limited use as discussed previously. The rapid flow thermal method has allowed the determination of the heat of reaction in some instances as well as reaction kinetics. It was considered to be worthwhile to use Roughton's rapid thermal method to study the kinetics of homogeneous liquid phase reactions. In this approach the experiment could be designed in such a way that the diffusion influence is negligible, and thus a true reaction kinetics for the oxidation of sodium dithionite can be established.

1.4. Present Work

The objective of this work has therefore been (a) to determine the rate data of the homogeneous liquid phase oxidation reaction of sodium dithionite in wide ranges of temperature, pH, and reactant concentrations (b) to study the effect of inhibitors such as manganese chloride,manganese

sulfate and triethanolamine as inhibitors and and (c) to establish a reaction mechanism of dithionite oxidation.

In this investigation, measurements were made of the homogeneous reaction rate by a flow thermal method.

CHAPTER 2

EXPERIMENTAL APPARATUS AND PROCEDURE

The entire equipment was designed and fabricated for studying the kinetics of fast homogeneous liquid phase reactions using a flow thermal method. The details of the experimental set up followed by the experimental procedure are given below.

2.1 Overall Description

The schematic flow diagram of the experimental set up is shown in Figure 1.

The basic elements of the set up are the storage tanks, thermostatic bath, control valves, flowmeters, mixer and an observation tube. The liquid storage tanks and all the metal parts of the equipment except the thermostatic bath were fabricated from 316 stainless steel. The constant temperature water bath was fabricated from brass. The mixing chamber and the reactor were constructed from plastic, so that the reactant solution did not come in contact with metal in the part of the apparatus where the rate measurements were made. All liquid lines and the outlet from the observation tube were made 3/8 inch o.d. Swagelok type tube fittings made out from polypropylene and Globe needle valves made out from 316 stainless steel were used in the

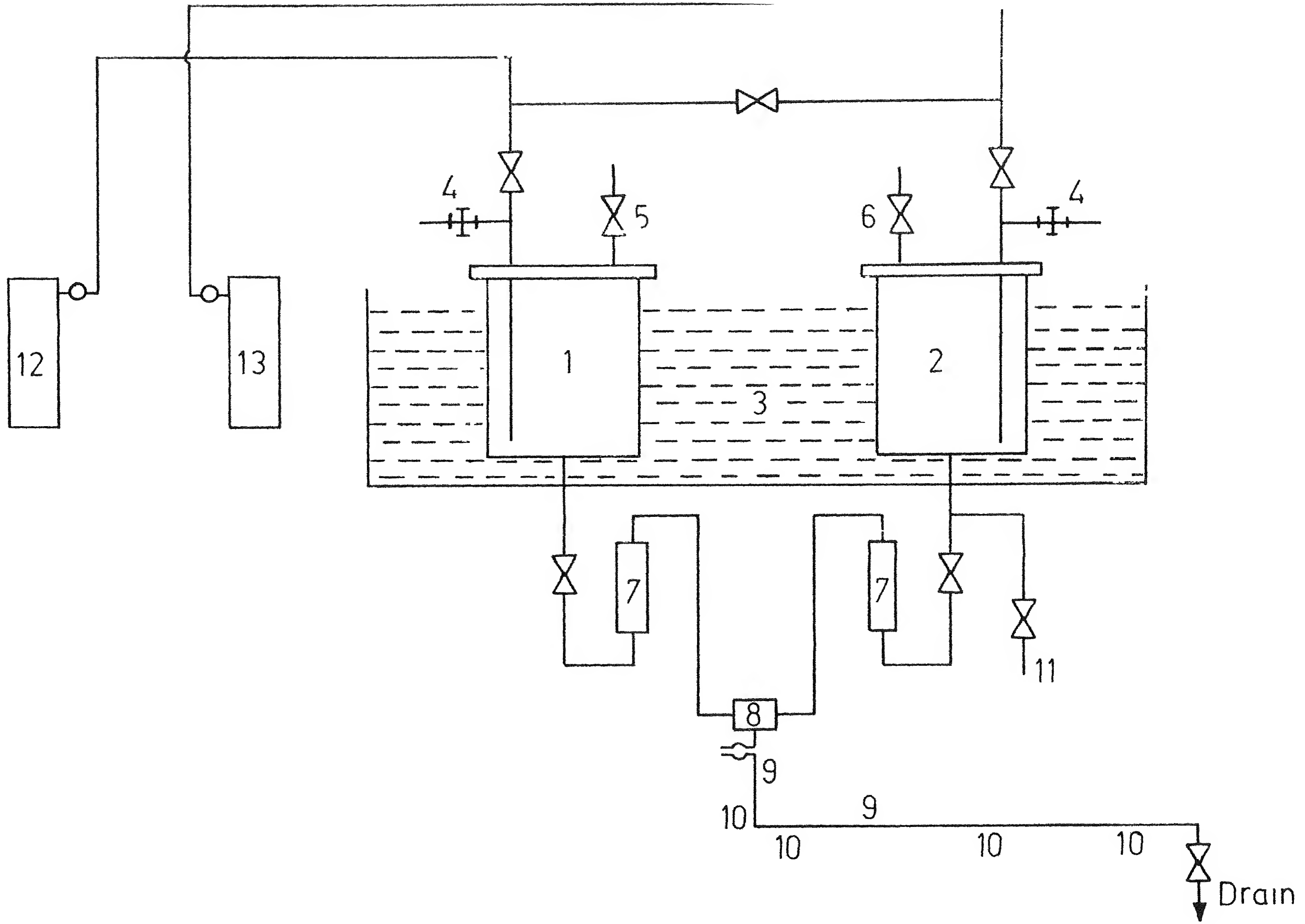

Fig 1 -Flow diagram of experimental apparatus

Key to Figure 1

1. Dithionite Feed Tank
2. Oxygen Feed Tank
3. Constant Temperature Water Bath
4. Safety Valves
5. Dithionite Feed Valve
6. Distilled Water Feed Valve
7. Rotameter
8. Mixer
9. Observation Tube
10. Thermocouple
11. Oxygen Sample Tap
12. Nitrogen Supply Cylinder
13. Oxygen Supply Cylinder

equipment. The following capabilities and characteristics are provided for:

1. The flow rate can be controlled to vary less than 1 per cent.
2. The temperature of the thermostatic bath can be controlled to within $\pm$ 0.1°C.
3. Mixing is extremely rapid.
4. Output response from the thermocouples is measured by means of Keithley Model 149 Microvoltmeter with a quick response and good stability.
5. Increased concentration of oxygen could be obtained by operating the system at elevated pressure.

2.2 Observation Tube

The observation tube consisted at length of 1/4 inch o.d. by 1/8 inch i.d. plexiglass tubing. It was connected to the mixing chamber by means of a plastic male connector. A number of Swagelok type tees made out from polypropylene were provided to locate thermocouples in the observation tube. The outlet of the observation tube was connected to a 3/8 inch drain line through a needle valve to control the desorption of the dissolved gas, if any. The reactor was wrapped with approximately two inches of Fiberglass and Asbestos insulation to minimize heat transfer to the surroundings.

2.3 Mixing Chamber

The mixer, as shown in Figure 2 was constructed from a 4"x1"x1" block of plexiglass. The two fluid streams entered the mixer in opposite direction through 3/8'' to 1/8'' reducers, whence they were ejected into the mixing chamber as two jets. Due to the turbulence created in the mixer, mixing was completed in an extremely short time. One outlet of the mixing chamber was connected to observation tube while the other was used to locate thermocouples at the mixing points. The mixer was insulated with approximately two inches of fiberglass and asbestos insulation.

2.4 Temperature Measurements

The different measurements of the temperature were made by employing pairs of thermocouples opposed in series to give increased response to the small temperature ranges. The wires of the thermocouples were used to transmit potential difference to the microvoltmeter. The details of the thermocouples are described below.

Extreme care was required in preparing the thermocouples which were to be inserted in the reactor since they were required to withstand upto 50 psig and to function properly in alkali and aqueous salt solutions. The thermocouples were made of 24 gauge copper and constantan wires. The hot junction of the thermocouple was made by wrapping

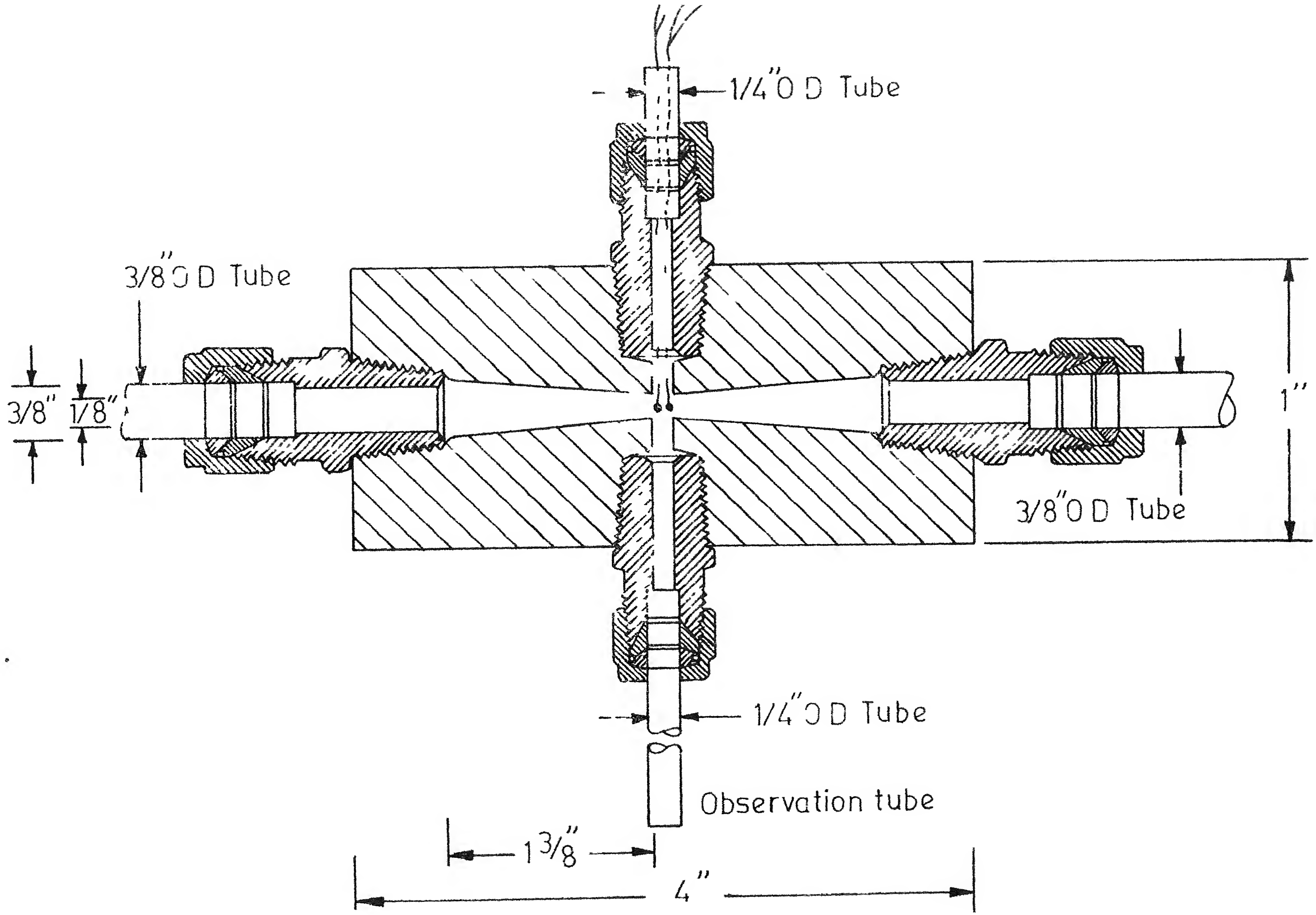

Fig 2 - Crossectional view of mixing chamber.

one wire about the other for a short distance and then joining the wires together by fusion with an electric arc. Four such thermocouples were made and connected opposite in series. Each lead from the pair of thermocouple junctions was inserted in a 1/4 inch plexiglass tube which was then sealed with epoxy resin cement. The thermocouple junctions and immersion leads which were exposed to the alkali or salt solution also were coated with epoxy resin. The thermocouple inserts thus formed were then placed into the mixing chamber and the observation tube through a male connector and a tubing tee, respectively. The thermocouples were calibrated against a 25 ohm Leeds and Northrup platinum resistance thermometer and Muller bridge assembly. The procedure and calibration curve are presented in Appendix A.

2.5 Pressurized Storage Tanks

Two stainless steel tanks with a capacity of six liters each, were used to store and supply two feed solutions, one of oxygen dissolved in distilled water and other of an aqueous solution of sodium dithionite, to the mixing chamber at constant pressure. Nitrogen was used to pressurize the tanks and on occassion to stirr the dithionite solution by bubbling through the tank. The tanks were provided with a pressure tight flange at the top with two holes fitted with 3/8 inch valves and fittings, one for charging feed

solution and other for admitting gas. Safety valves were provided at the top of the storage tanks as shown in the flow diagram, Figure 1. Both the tanks were kept in a constant temperature water bath. The male connectors of the glass lines were bore to pass 3/8 inch stainless steel tubing from the valves to one inch above the base of the storage tanks to bubble the gas or to stirr the solution by nitrogen through the tubing. The oxygen supply cylinder was directly connected to its feed tank where as a nitrogen supply cylinder could be connected either to dithionite feed tank or both the storage tanks, depending upon whether used as a stirring medium or to pressurize the system. Flexible copper tubing connected the regulators of the supply cylinders to the valves of the feed tanks.

Oxygen was bubbled into the feed tank containing distilled water under pressure, thereby producing a solution of dissolved oxygen. The two solutions were forced by admitting nitrogen pressure to pass through the mixing chamber. Valved inlets for charging feed solutions were used as vents cracking slightly to allow the oxygen to bubble slowly through the water and nitrogen to stirr the dithionite solution.

The bottom of the storage tanks were connected by 3/8 inch o.d. stainless steel tubes which were provided with control valves. This was again connected to the inlets of

of the mixing chamber via flow meters. These tubes were wrapped with approximately two inches of fiberglass and asbestos insulation to minimize heat transfer to the surroundings.

2.6 Constant Temperature Control

Constant temperature water bath was used to maintain a constant temperature for both storage tanks. A Jumo-German contact thermometer, 0-100°C, which was dipped in the bath and connected to a relay device, was used along with a Remmi-Stirrer and a precision thermometer to control the bath temperature to an accuracy of ± 0.1°C.

2.7 Flow Rate Measurements

Gilmond flow meters were used to measure the flow rates. The flow meter for dithionite solution provided a flow range 0 to 16 ml per second while that for oxygen solution provided a flow range of 0 to 35 ml per second. The accuracy of the flow meters was ± 1 per cent of full scale.

The reliability of the equipment has been checked using the NaOH-CO_2 system [39,40]. The average of the second order rate constant agreed within 5 per cent with the value reported by Pinsent et al. [36].

2.8 Experimental Procedure

2.8.1 Uninhibited Runs

Before each run, distilled water was charged to tank 2 and the oxygen was bubbled through the tank at a pressure for desired concentration for four to five hours to produce an oxygen solution. Sodium dithionite of the desired concentration was charged to the other tank. It was also allowed for four to five hours to attain temperature equilibrium. The sodium dithionite solution was occasionally stirred with nitrogen.

Microvoltmeter was stabilized by turning it on half an hour before taking readings.

After the temperature equilibrium was attained the tanks were pressurized by nitrogen to 50 psig. Firstly, each solution was allowed to pass separately in order to set the microvoltmeter to zero reading with the help of zero suppress knobs to account for any temperature change due to friction or heat transfer to the surroundings. Then, both the solutions were allowed to pass through the rotameters to the mixing chamber, and hence down the reactor, where the reaction occurred. Flow rates were adjusted to provide the desired ratio of the two reactant streams. A steady value of the differential e.m.f. from the thermocouples located at the mixing points and a point along the observation tube was obtained within seconds on the microvoltmeter.

The overall time required for a completed run was about 20-40 seconds.

The concentration of sodium dithionite was determined by the iodimetric[41] method. The method is based upon the fact that when sodium hydrosulfite ($Na_2S_2O_4$) is added to an excess of formaldehyde, the sodium hydrosulfite couples with the formaldehyde to form the stable sodium formaldehyde sulfoxylate which is then titrated with iodine. From this titration the percentage of $Na_2S_2O_4$ is readily calculated.

The reagents used for this analysis were iodine solution (0.1N), formaldehyde solution (pH=9) and acetic acid solution (20 per cent).

The determination of absorbed oxygen in water was made by Winkler's method [42]. First of all, 1 ml of potassium iodide and 1 ml of manganese chloride solutions were added to the sampling bomb. Just prior to taking the sample of the oxygen stream the bomb was evacuated for two minutes. The bomb was attached to the sample point, and the sample was gradually admitted to the bomb under elevated pressure. By measuring the weight of the bomb before and after the solution was passed in, the weight of solution added in the bomb was known.

The dissolved oxygen reacted with the reagents in the sampling bomb forming an intermediate precipitate. The contents of the bomb were transferred to an Erlenmeyer flask

and boiling distilled water was rinsed through the sample bomb and added along with 3 ml of concentrated hydrochloric acid to the Erlenmeyer flask. This acid dissolved the precipitate readily with liberation of iodine which was titrated with sodium thiosulfate.

The runs were carried out at 30°C. The average concentration of sodium dithionite varied from 3.85×10^{-5} to 1.0×10^{-1}M and oxygen concentration from 5×10^{-4} to 3×10^{-3}M. The apparent activation energy was determined by varying the temperature between 30 and 90°C. The pH was maintained at a constant value of 11 by addition of small amounts of alkali. The pH was varied from 8 to 11 to study the effect of pH on reaction rate. The measurements of pH were made with the help of Philips PR 9405 M precision pH meter.

2.8.2 Inhibited Runs

The experimental technique was essentially the same as that for uninhibited runs. Manganese chloride, manganese sulfate and triethanolamine were used as the inhibitors in the present study. The inhibitor was added in equal strength to both the storage tanks in order to get constant average molar inhibitor concentration. The inhibitor concentration needed for an experiment was taken from a strong solution of known concentration and diluted with distilled water.

Most of the experiments were carried out at a dithionite concentration of 7.7×10^{-5}M, oxygen concentration of 1.2×10^{-3}M and inhibitor concentration of 1.0×10^{-3}M at a temperature of 30°C. In order to study the effect of inhibitor on the reaction rate, the concentration of inhibitor was varied from 1.0×10^{-4} to 1.0×10^{-2}M. The concentration of dithionite varied from 3.85×10^{-5} to 1.0×10^{-1}M and oxygen concentration from 5.0×10^{-4} to 3.0×10^{-3}M for the purpose of determining the reaction order in dithionite and oxygen, respectively. The pH was maintained at a constant value of 8 to study the effect of inhibitor concentration on the reaction rate. In other cases the pH was kept as 11. The reaction temperature for all inhibited runs was 30°C.

All experimental data for uninhibited and inhibited runs are presented in Appendices B to E.

CHAPTER 3

RESULTS AND DISCUSSION: UNINHIBITED RUNS

The experimental data for uninhibited runs have been presented in Appendix B.

In most of the experiments the dithionite was completely consumed (Tables 4, 8 and 10, Appendix B) as evidenced by the plateau reached in the temperature profile along the observation tube. The energy liberated by reaction raised the temperature of the solution and the total temperature rise was measured. The oxygen concentration, M, was determined by the energy balance $\Delta H_R x M = \Delta T x Cp$. The mean heat capacity, Cp, of the solution was that of water since the dithionite concentration was low, e.g., the range was from 3.85×10^{-5} M to 1.0×10^{-1}M.

The experimental data were obtained as potential differences along the observation tube. Plotting temperature difference versus residence time indicated linear relationship. Typical examples of the change in temperature as a function of residence time (runs RD-2, RD-5) are shown in Figure 3. The rate of oxygen consumption was calculated from the slope of such lines. A sample calculation (for run RD-2) is given in Appendix B.

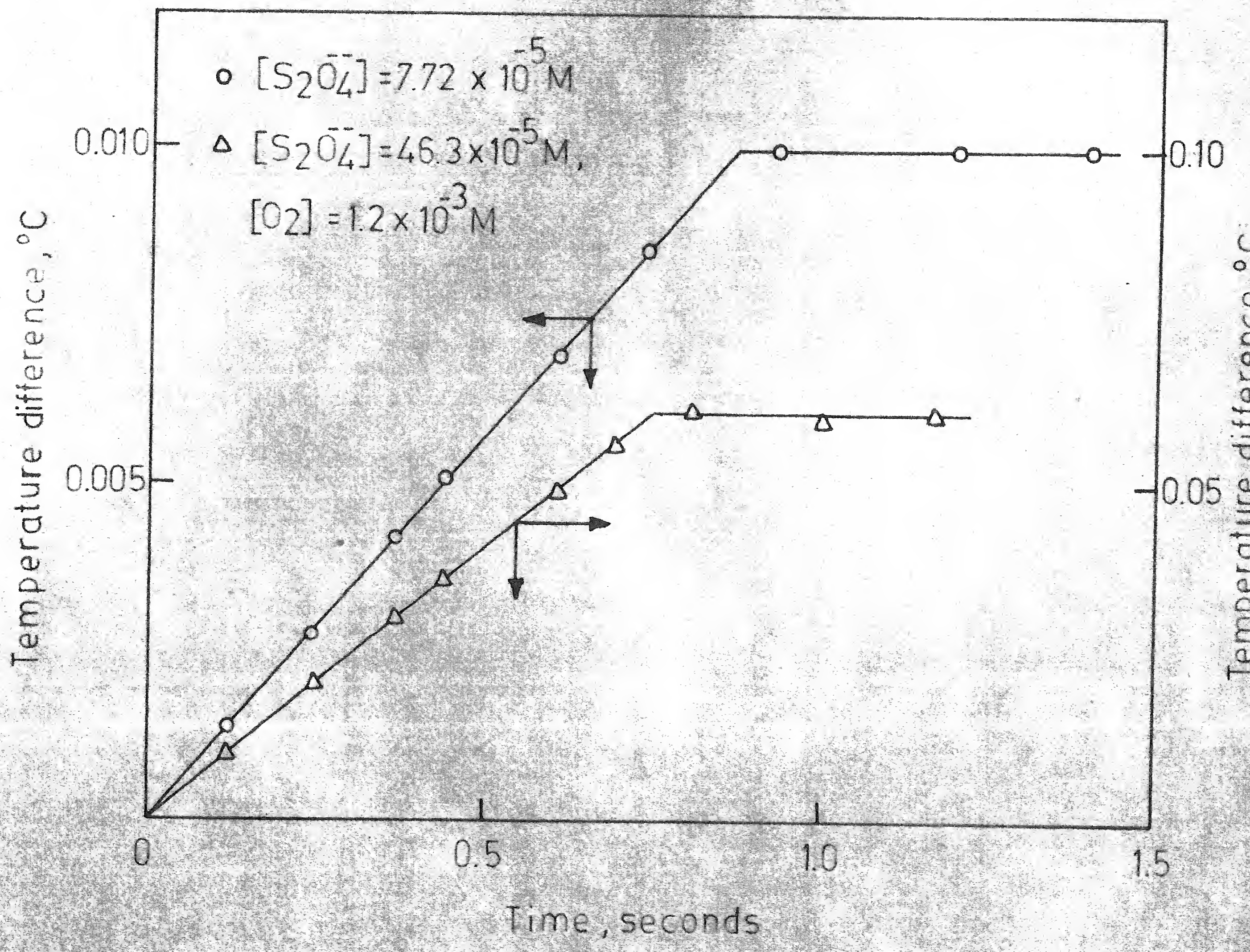

Fig. 3 - Typical temperature profiles as a function of time of reaction at 30°C pH = 11

The overall stoichiometry for the oxidation of dithionite has been described [3,4,7] by the equation

$$Na_2S_2O_4 + O_2 + H_2O \rightarrow NaHSO_3 + NaHSO_4 \qquad (3.1$$

The standard enthalpy of reaction is -135.1 ± 8 kcal/g-m of oxygen reacted [43, 44].

From the plots (Figure 3) one can observe the straight lines with different slopes upto the point where dithionite was completely consumed. The temperature corr ponding to this point resulted in the heat of reaction of -130.1 ± 9.9 kcal/ g-mole which approximately corresponde to the enthalpy of the overall reaction given by Equation (3.1). Table 1 gives the calculated enthalpy for all the runs where the plateau was reached. The present results clearly establish the stoichiometric Equation (3.1), withi experimental error.

It is not the intention at this time to enter into analyses in detail of the determination of the heat of reaction, but rather to offer the stoichiometry as means of calculating the rate of reaction. All the calculations reported in this thesis are based on a ΔH_r = -135.1 kcal/ mol of oxygen reacted.

3.1 Effect of pH on Reaction Rate

It has been reported by several authors [5,6] that

TABLE 1: ENTHALPY OF DITHIONITE OXIDATION

Run No.	In Reactor: Average dithionite conc. (M)	In Reactor: Average oxygen conc. (M)	Maximum rise in temperature, (°C)	$-\Delta H_{298}$ Kcal/g-mole
RP-1	3.85×10^{-5}	0.0012	0.0049	128.6
RP-2	3.85×10^{-5}	0.0012	0.005	129.9
RP-3	3.85×10^{-5}	0.0012	0.005	129.9
RP-4	7.72×10^{-5}	0.0012	0.010	129.5
RP-5	7.72×10^{-5}	0.0012	0.011	142.5
RP-6	7.72×10^{-5}	0.0012	0.010	129.5
RP-7	38.50×10^{-5}	0.0012	0.050	129.9
RP-8	38.50×10^{-5}	0.0012	0.050	129.9
RP-9	38.50×10^{-5}	0.0012	0.049	127.3
RP-10	7.71×10^{-4}	0.0012	0.100	129.7
RP-11	7.71×10^{-4}	0.0012	0.097	125.8
RP-12	7.71×10^{-4}	0.0012	0.100	129.7
RD-1	3.85×10^{-5}	0.0012	0.005	129.9
RD-2	7.72×10^{-5}	0.0013	0.010	129.5
RD-3	23.17×10^{-5}	0.0013	0.030	129.5
RD-4	38.57×10^{-5}	0.0012	0.050	129.6
RD-5	46.28×10^{-5}	0.0014	0.060	129.6
RD-6	61.66×10^{-5}	0.0015	0.083	134.6
RD-7	77.80×10^{-5}	0.0013	0.100	128.5
RT-1	7.72×10^{-5}	0.0012	0.010	129.5
RT-5	7.72×10^{-5}	0.0012	0.010	129.5
				$\Delta H_{298} = 130.1 \pm 9.9$

the reaction rate in low pH range was high enough to have meaningful measurements. In alkaline medium, however, it was found that the rates were measurable and that is why most of these authors conducted the experiments in alkaline medium. However, no detailed study of the variation of pH was made for the oxidation of dithionite.

In the present work a number of experiments were performed at various pH [8-11] values of reactant solutions to demonstrate its effect on reaction rate at 30°C. The data are presented in Tables 4, 5, 8 and 9, Appendix B. The dithionite concentration was kept constant at four different values in the range of 3.8×10^{-5} to 7.7×10^{-4}M. For all runs the oxygen concentration was kept as 0.0012 M. The results are shown in Figures 4 and 5.

The experimental results show that rate decreases with the increase in pH values. It is possible that dithionite undergoes hydrolysis [45] which would partially remove dithionite ion from the reaction medium reducing thereby its effective concentration available for oxidation reaction. The higher the concentration of OH^- ions i.e. increased values of pH, greater would be the extent of hydrolysis reaction resulting in increased depletion of dithionite concentrations and thus decreasing the rate of oxidation effectively.

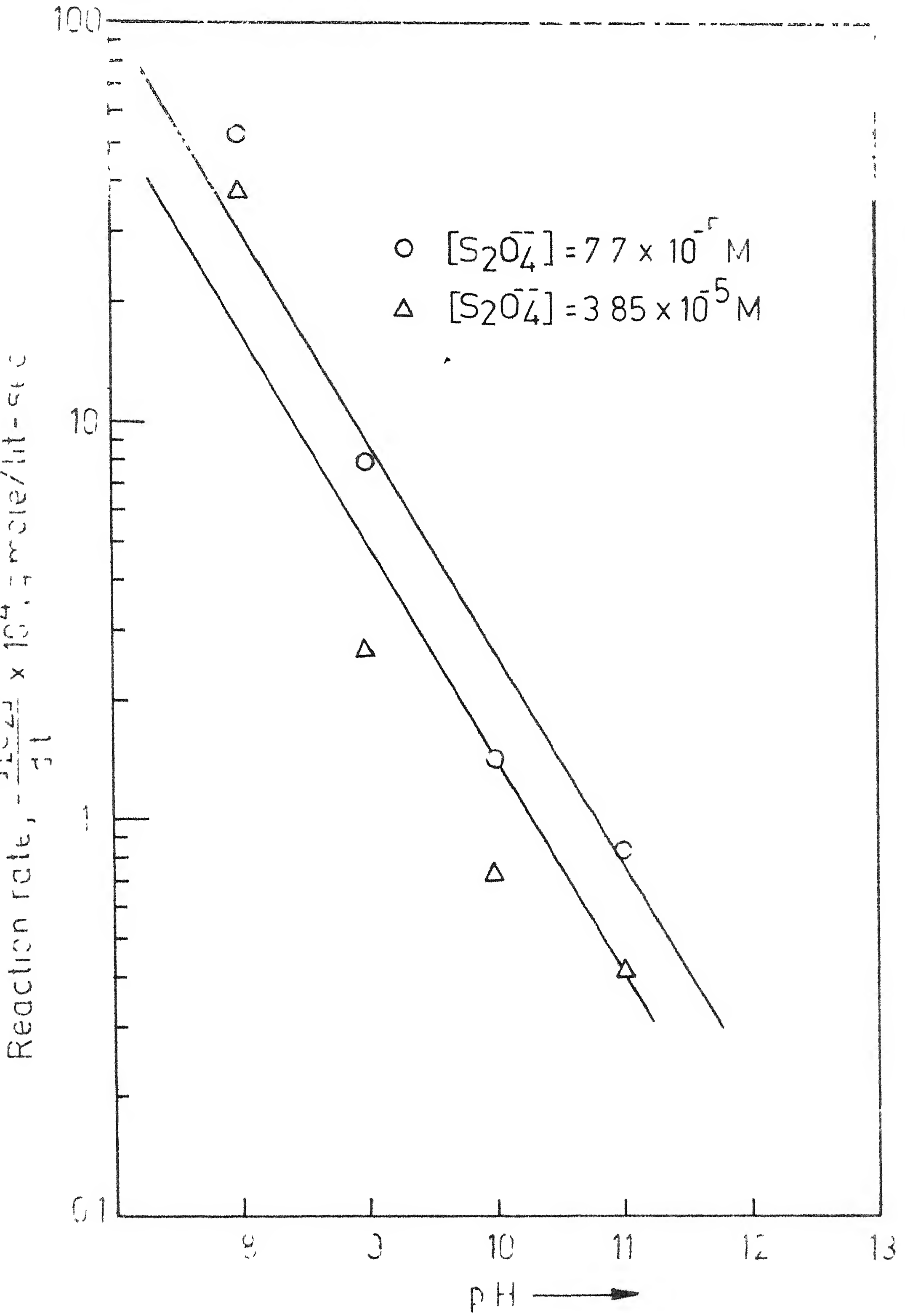

Fig 4 - Effect of pH on reaction rate at 30°C, $[S_2O_4^{--}] = 3.85 \times 10^{-5}$ and 7.7×10^{-5} M

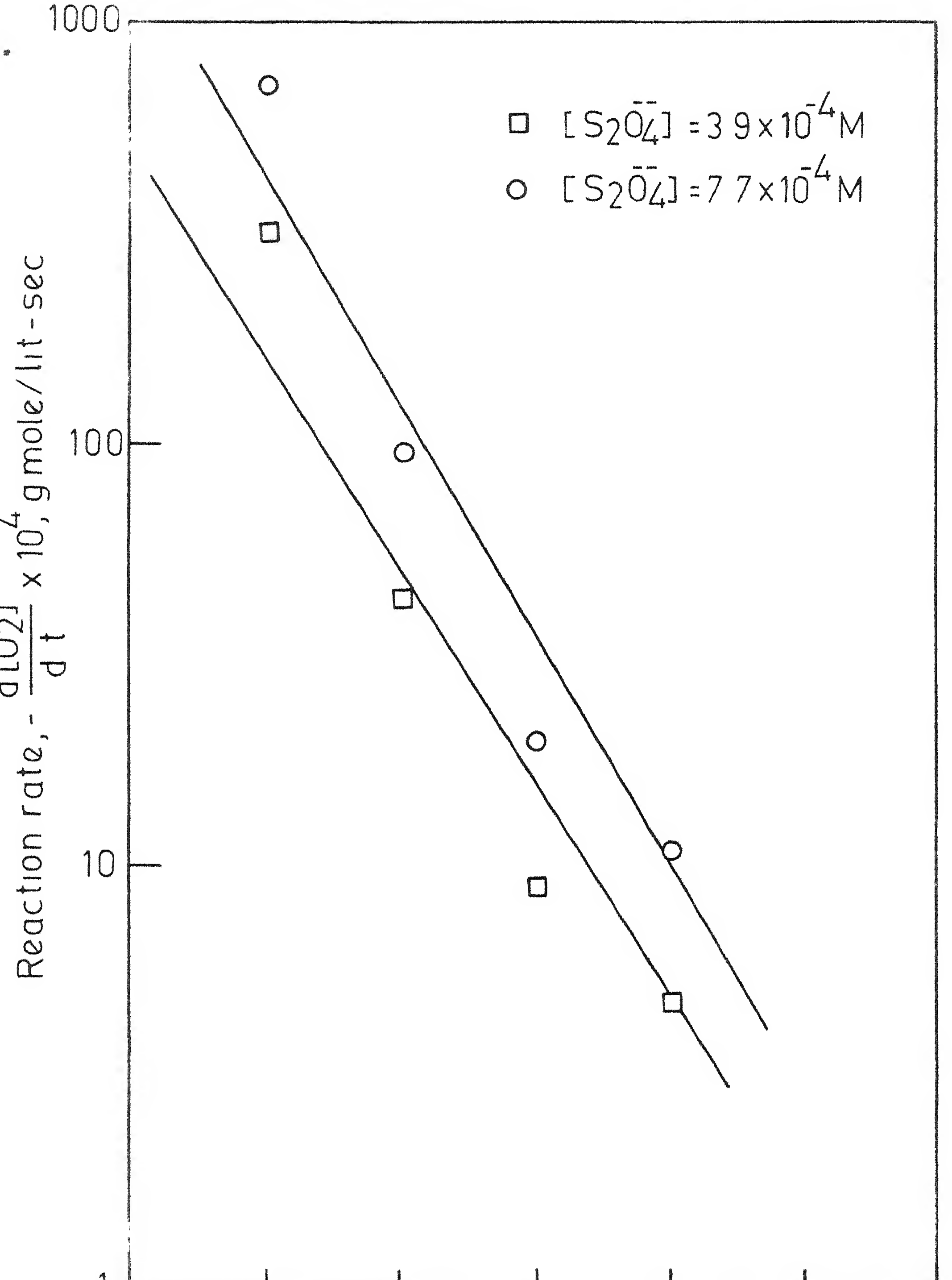

Fig 5 - Effect of pH on reaction rate at 30°C, $[S_2O_4^{--}] = 3\ 9 \times 10^{-4}$ and $7\ 7 \times 10^{-4}$ M

3.2 Effect of Oxygen Concentration

Tables 6 and 7, Appendix B give the rate data for the effect of oxygen concentration on the reaction rate for uninhibited runs. All the experiments were conducted at $30^{o}C$ and pH = 11. The oxygen concentration was varied keeping the dithionite concentration constant. The range of variation of oxygen concentration was from 5.4×10^{-4} to 3.0×10^{-3}M. Four dithionite concentrations were chosen for this study in the range of 3.8×10^{-5} to 1.0×10^{-1}M.

The relation of rate versus oxygen concentration is shown in Figure 6. Horizontal lines show that over a wide range of oxygen concentration, the reaction rate was found to be independent of oxygen concentration. This is in agreement with the results of previous investigators[6,7].

3.3 Effect of Dithionite Concentration

To study the effect of dithionite concentration on the rate of reaction, a number of experiments were performed at various dithionite concentrations. The data have been presented in Tables 8 and 9, Appendix B. The reaction conditions were maintained at a temperature of $30^{o}C$ and pH of 11. The concentrations of dithionite ranged from 3.8×10^{-5} to 1.0×10^{-1}M. The rate of oxygen consumption is shown as a function of average dithionite concentration in Figure 7. All the data shown in this figure correspond

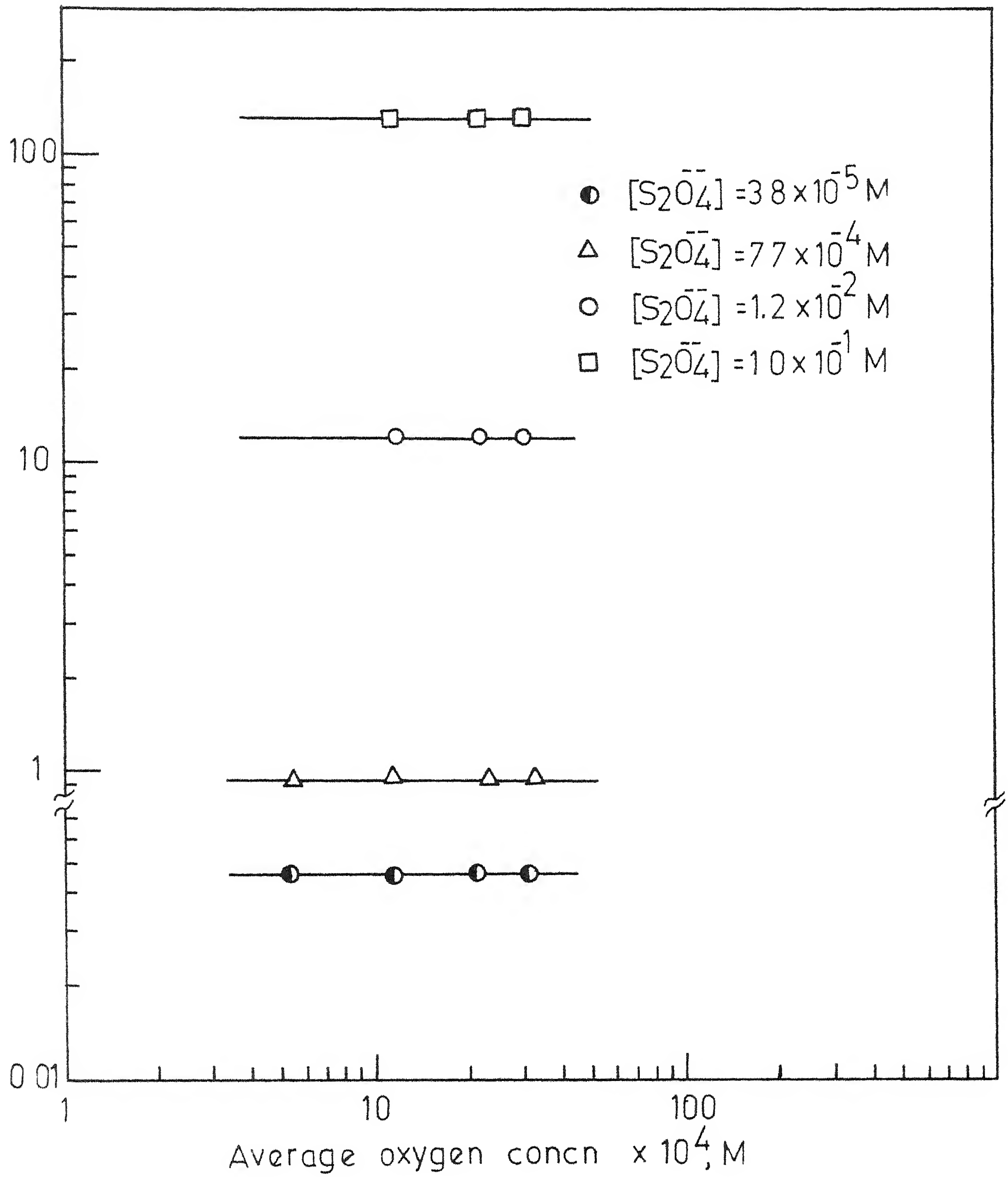

Fig 6 - Effect of oxygen concentration on reaction rate at 30°C, pH = 11

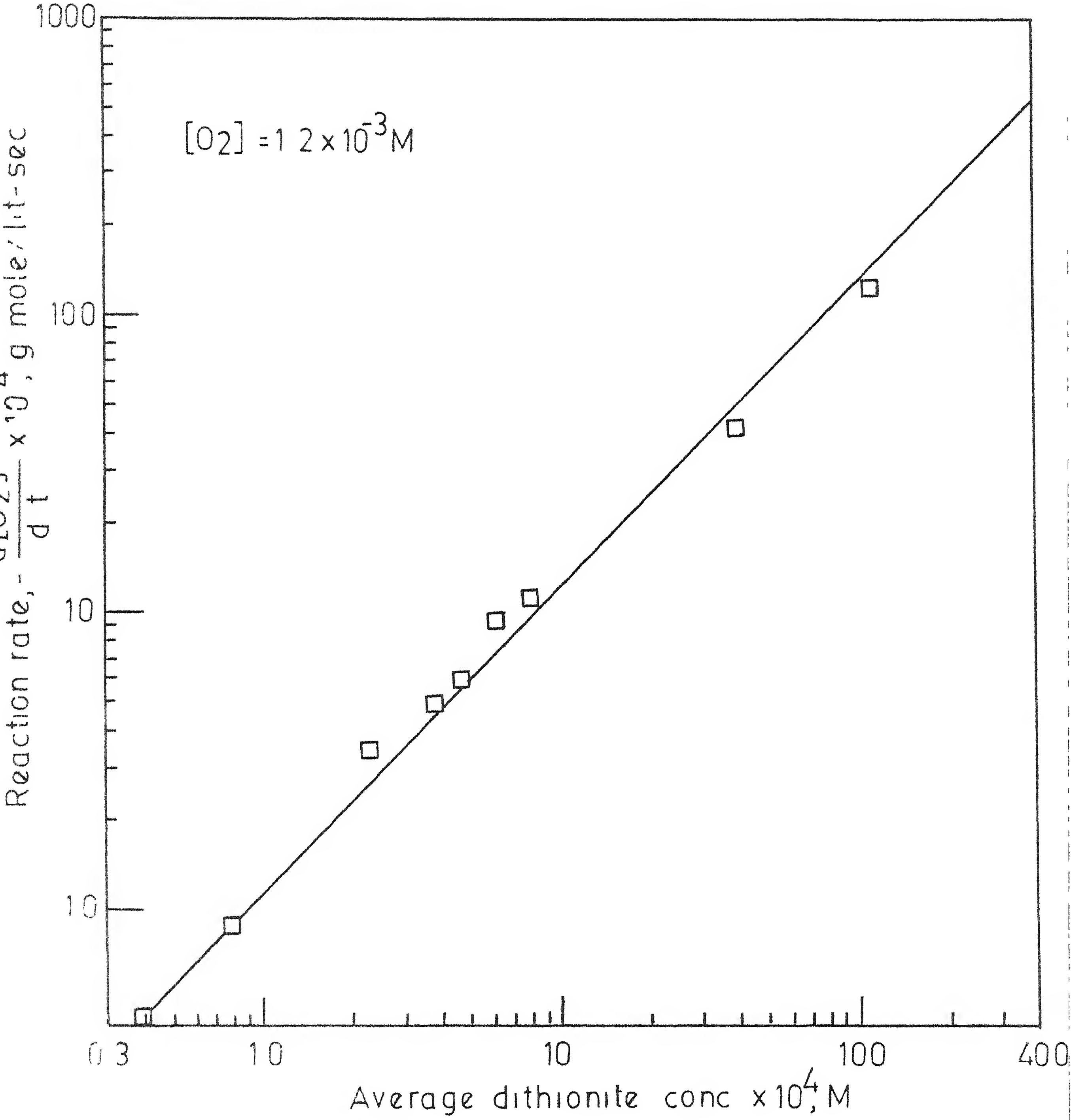

Fig 7 -Effect of dithionite concentration on reaction rate at 30°C, pH = 11

to an average oxygen concentration of 0.0012 M. Rate against dithionite concentration resulted in one power relation. The first order rate constant calculated was 1.3 sec^{-1} with a standard deviation of 0.1.

As part of physiological studies in terms of oxygen absorption in haemoglobin Morello et al. [6] studied the rate of reaction of dithionite ion with oxygen in aqueous solutions employing the rapid mixing apparatus. The oxygen concentrations during the course of reaction were measured by a polarographic technique. The initial range of dithionite concentrations were from 8×10^{-5} to 4.7×10^{-4} M while the oxygen concentration was 10×10^{-5} M. They reported that the reaction was first order with respect to dithionite and zero order with respect to molecular oxygen. This is in complete agreement with the results of present study. Morello et al. [6] further indicate that the first order rate constant would have an initial value greater than 42 $sec.^{-1}$ at a pH of 7 or 8. The rate constant calculated on the basis of present experiments at a pH of 8 comes to a value of 69 sec^{-1}.

Rinker et al. [5] studied the air oxidation of sodium dithionite in aqueous solutions which was 0.1 M in sodium hydroxide. The initial concentrations of dithionite varied from 5×10^{-3} to 20×10^{-3} M. Under conditions in which diffusion of air was not controlling the rate the authors

observed that the oxidation was half order with respect to dithionite. These results are in disagreement with the present findings. It is interesting, however, to compare the reaction rates at compatible dithionite concentrations and pH values with the assumption that oxygen concentration does not affect the reaction rate. The interpolated value of the reaction rate at a dithionite concentration of 7.7×10^{-5} M from Rinkers et al. [5] data comes to approximately 4×10^{-6} M/sec. This would be at 0.1 M NaOH, or at a pH of 13. The extrapolated value of reaction rate at the dithionite concentration of 7.7×10^{-5}M from the curve of pH versus reaction rates (Figure 4) reads approximately 6×10^{-6} M/sec which is in good agreement with the value of Rinker et al.[5].

3.4 Apparent Activation Energy

In order to determine the apparent activation energy, experiments were carried out at five different temperatures in the range 30 - 90°C, while keeping the average concentrations of dithionite and oxygen approximately constant at 7.7×10^{-5} M and 0.0012 M respectively. The pH value was maintained as 11. The rate data are given in Tables 10 and 11, Appendix B. The logarithm of rate of reaction of oxygen was plotted with the inverse of absolute temperatures

at the temperatures of 30°, 45°, 60°, 75°, 90°C (Figure 8). The apparent activation energy for the overall oxidation was calculated to be 17.5 kcal per g-mole. This value of activation energy is typical of the values for homogeneous reactions [5, 46].

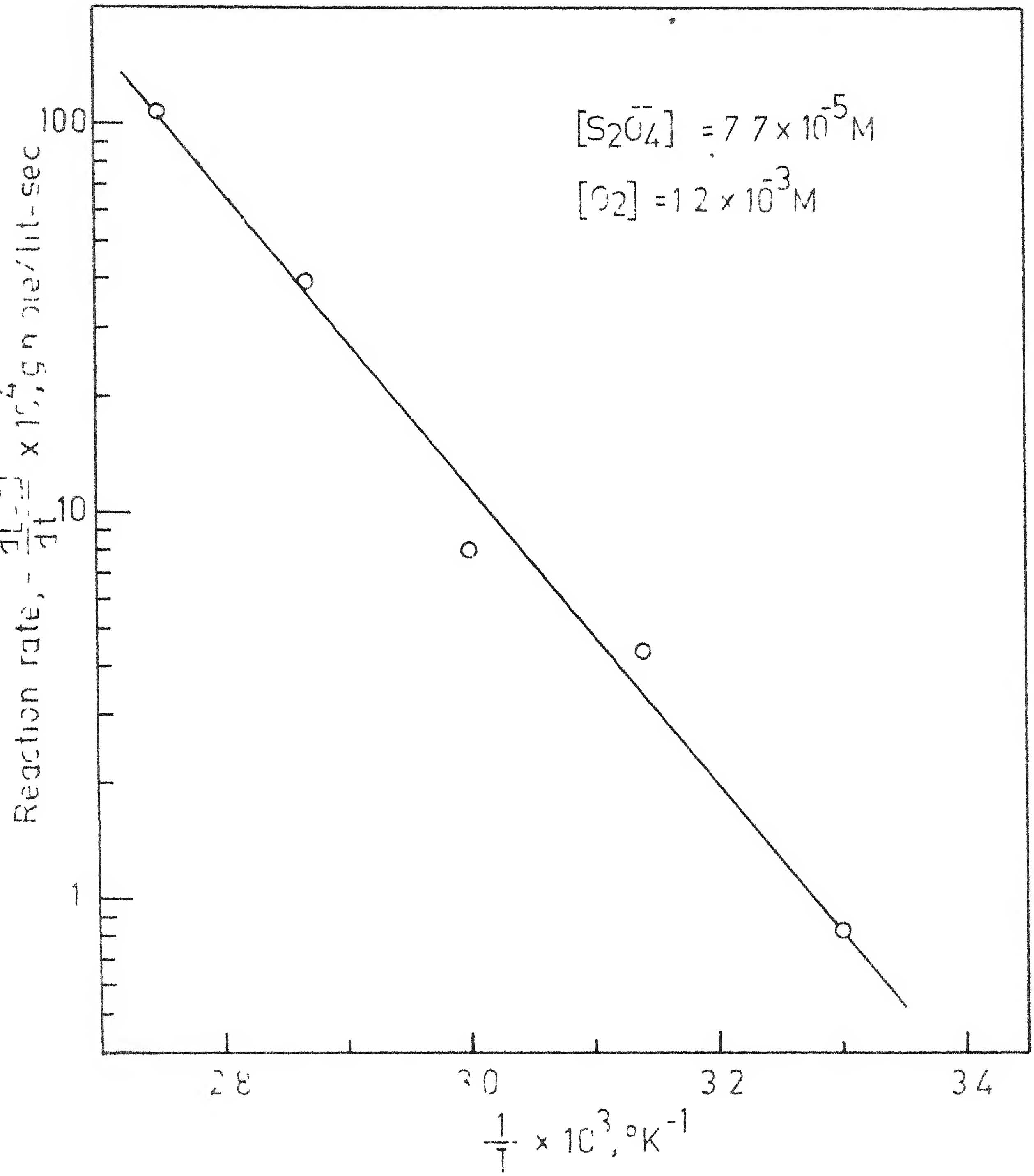

Fig 8 - Effect of temperature on reaction rate, pH=11

CHAPTER 4

RESULTS AND DISCUSSION: INHIBITED RUNS

The most significant feature of the dithionite oxidation is its marked sensitivity to inhibitors [8, 9, 38]. In fact, the dithionite oxidation proceeded remarkably slow when the inhibitors were added.

A study of the rate of oxidation versus the inhibitor concentration should give more precise information on the role of inhibitor in the free radical formation reaction. To clarify the dependence on the inhibitor a series of experiments were performed at approximately constant dithionite concentration of 7.7×10^{-5} M and inhibitor concentration in the range of 10^{-4} to 10^{-2} M. Appendices C, D and E contain all the recorded and calculated data in presence of inhibitors, manganese chloride, manganese sulfate and triethanolamine, respectively. Results and discussion of the inhibitors are described individually in the following:

4.1 Inhibition with Manganese Chloride

Sodium dithionite oxidation reaction was inhibited with mangane chloride. The experimental data for this study have been given in Tables 12-17, Appendix C.

Experiments were conducted to study the effect of $MnCl_2$, oxygen and sodium dithionite on the rate of this reaction at 30°C.

4.1.1 Effect of $MnCl_2$ Concentration

To clarify the dependence of $MnCl_2$ on the rate of dithionite oxidation, experiments were performed at constant average dithionite and oxygen concentrations of 7.7×10^{-5}M and 1.2×10^{-3} M, respectively. The $MnCl_2$ concentration for these experiments varied from 1.0×10^{-4} M to 1.0×10^{-2}M The pH was kept at 8. The experimental data are given in Tables 12 and 13, Appendix C. The results of these experiments are shown in Figure 9. The apparent order of the reaction with respect to $MnCl_2$ concentration was found to be 0.8.

4.1.2 Effect of Oxygen Concentration

At a constant concentration of 7.7×10^{-5}M for dithionite and 1.0×10^{-3}M for $MnCl_2$ the experiments at a pH of 11 were conducted for various oxygen concentrations in the range of 5.0×10^{-4} to 3.0×10^{-3} M. The experimental measurements and calculated data have been tabulated in Tables 14 and 15, Appendix C. Figure 10 gives the effect of oxygen concentration in the presence of $MnCl_2$ -

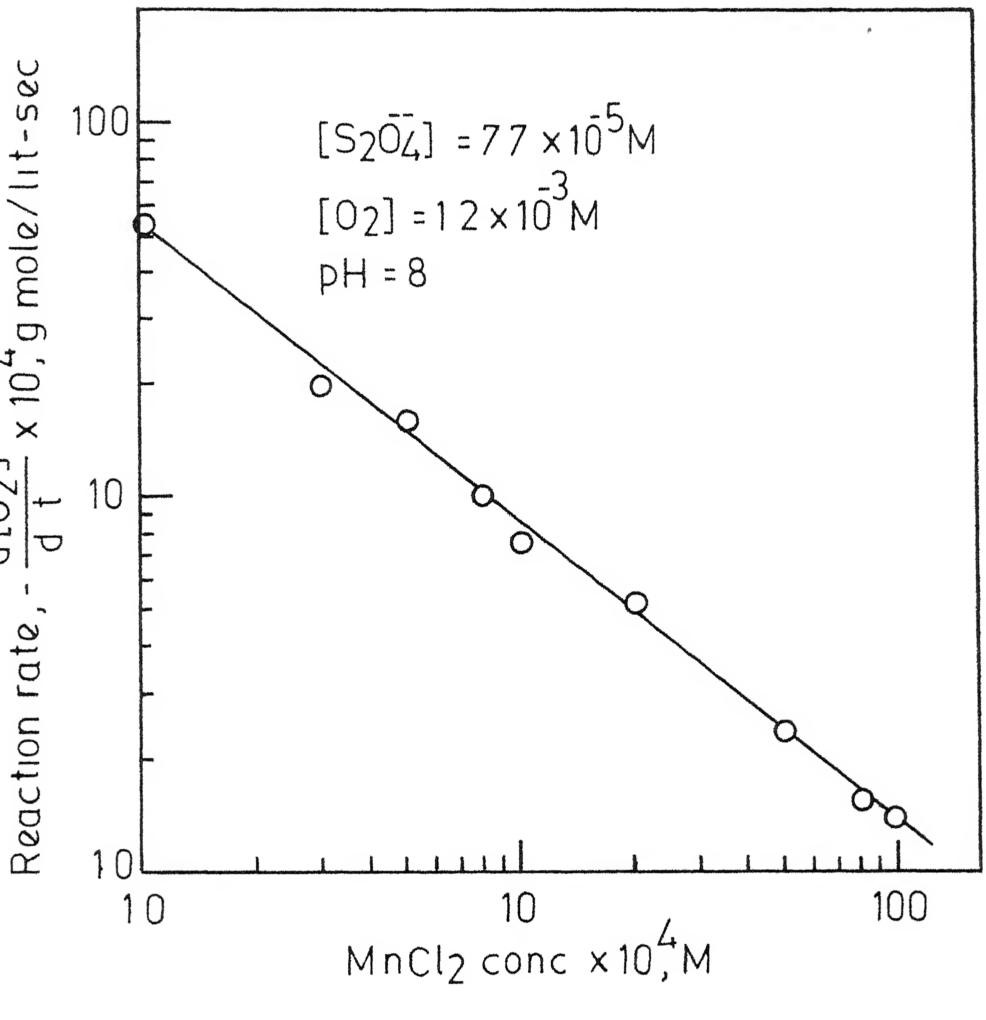

Fig 9 - Effect of $MnCl_2$ concentration at 30°C

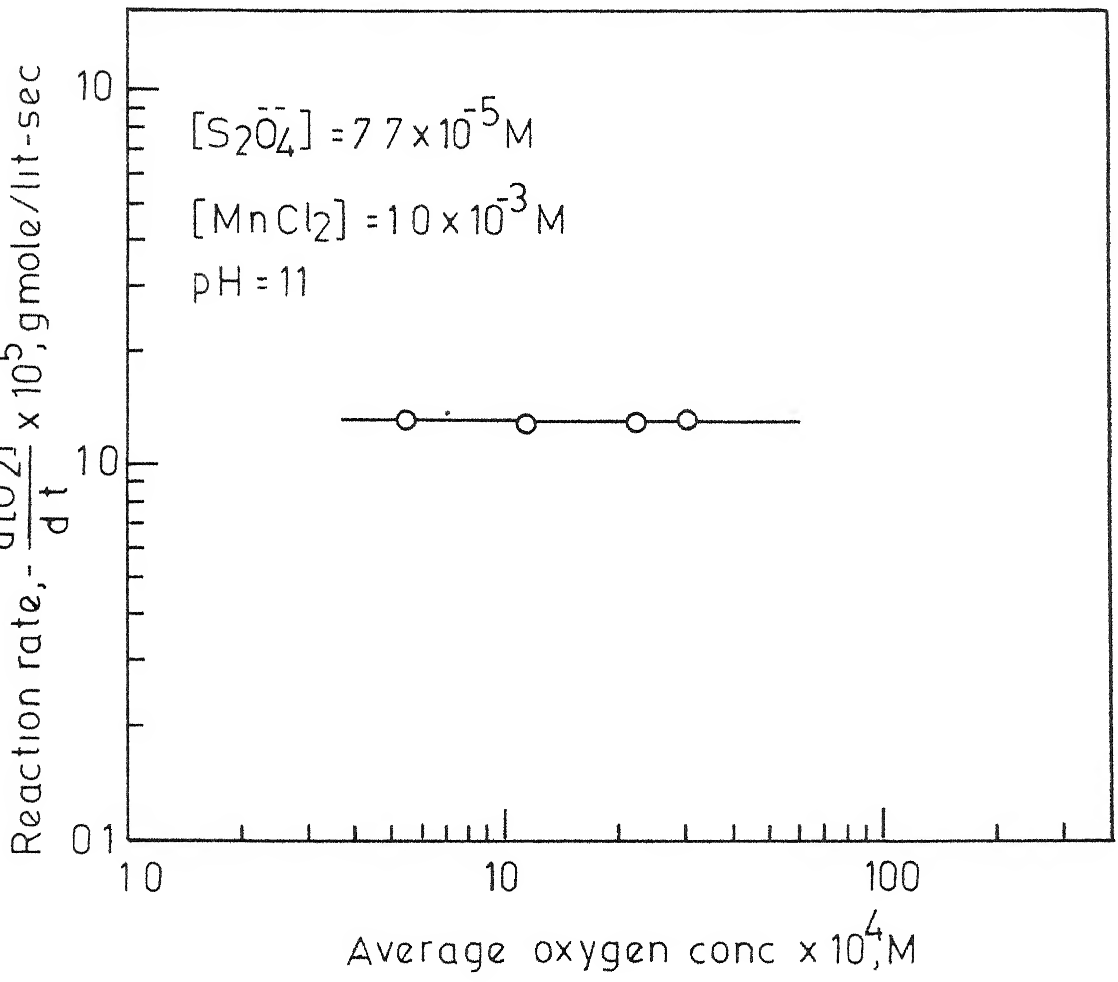

Fig 10 - Effect of oxygen concentration in presence of $MnCl_2$ at 30°C

inhibitor for dithionite oxidation. A zero order effect of oxygen concentration on reaction rate was found.

4.1.3 Effect of Dithionite Concentration

Tables 16 and 17, Appendix C present the experimental findings to demonstrate the effect of sodium dithionite on the rate of reaction in presence of $MnCl_2$ inhibitor. The concentrations of oxygen and $MnCl_2$ in all these experiments were kept constant at values of 1.2×10^{-3} M and 1.0×10^{-3} M, respectively. The dithionite concentration was varied from 3.85×10^{-5} M to 1.0×10^{-1} M. These experiments were conducted at a pH of 11. Figure 11 shows the rate of oxygen consumption as a function of average dithionite concentration. The rate resulted in one power relation.

4.2 Inhibition with Manganese Sulfate

Reaction conditions for dithionite oxidation in presence of $MnSO_4$ - inhibitor were approximately kept the same as for inhibition with $MnCl_2$ as in section 4.1. Recorded and calculated data for these experiments are given in Tables 18-23, Appendix D. The results are plotted in Figures 12, 13 and 14.

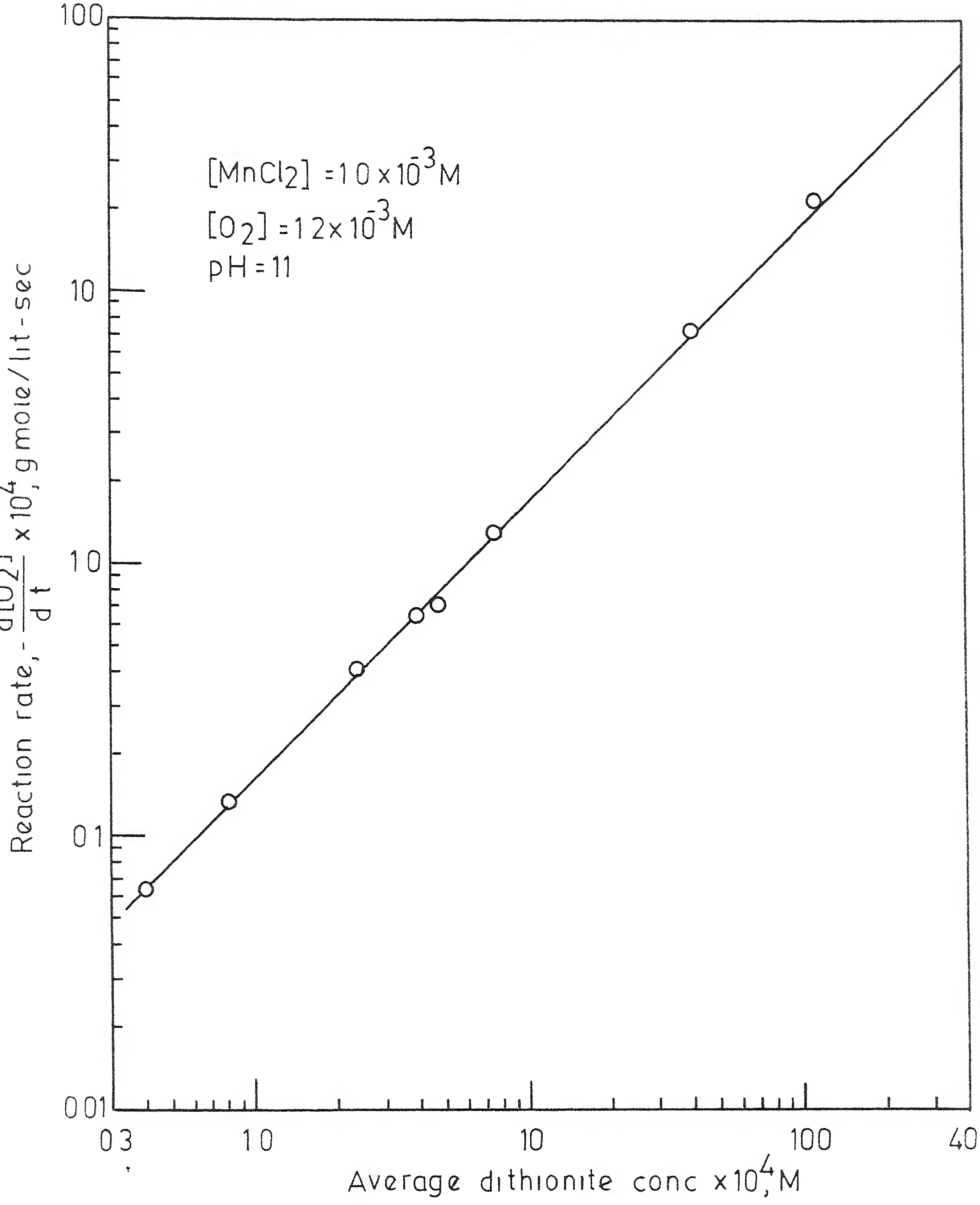

Fig 11 - Effect of dithionite concentration in presence

4.2.1 Effect of $MnSO_4$ Concentration

At a pH of 8 various experiments were conducted at constant concentrations of sodium dithionite and oxygen at values of 7.7×10^{-5} M and 1.2×10^{-3} M respectively. The range of $MnSO_4$ concentration variation was 10^{-4} to 10^{-2}M. Tables 18 and 19, Appendix D give the data for these experiments. Figure 12 shows that the order of reaction rate - variation with respect to $MnSO_4$ concentration is 0.9.

4.2.2 Effect of Oxygen Concentration

Experiments were conducted under the identical conditions as in 4.1.1 except that $MnSO_4$ was used in place of $MnCl_2$ to inhibit the reaction rate. Tables 20 and 21, Appendix D give the recorded and calculated data for these experiments. Figure 13 gives that there is no effect of addition of oxygen concentration on reaction rate.

4.2.3 Effect of Dithionite Concentration

The data for inhibited rates of dithionite oxidation with $MnSO_4$ are presented in Tables 22 and 23, Appendix D. Oxygen and $MnSO_4$ concentrations were kept as 1.2×10^{-3} M and 1.0×10^{-3} M, respectively. The reaction temperature was 30°C and pH of reactant solutions was 11. The dithionite

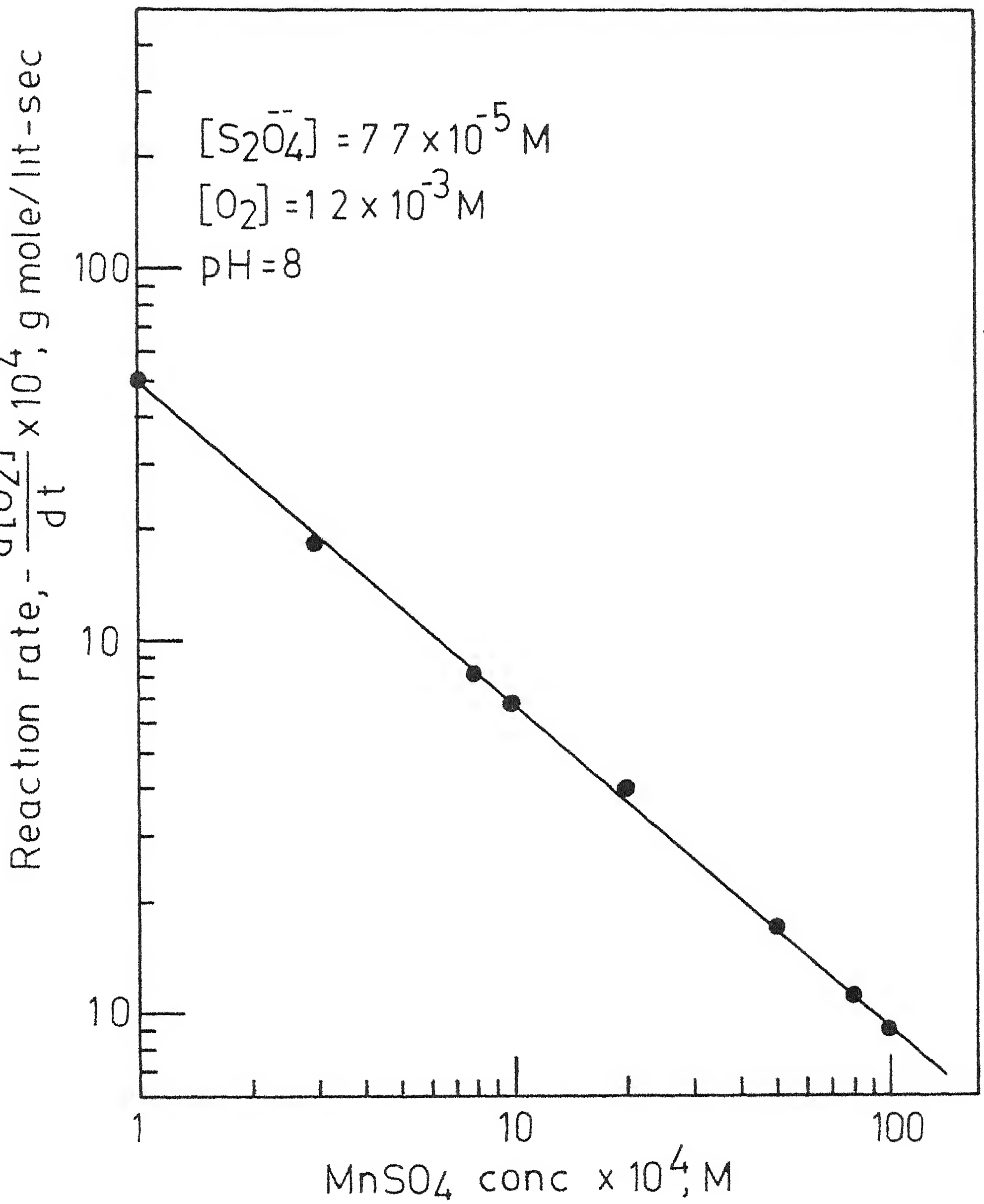

Fig 12 - Effect of $MnSO_4$ concentration at 30°C

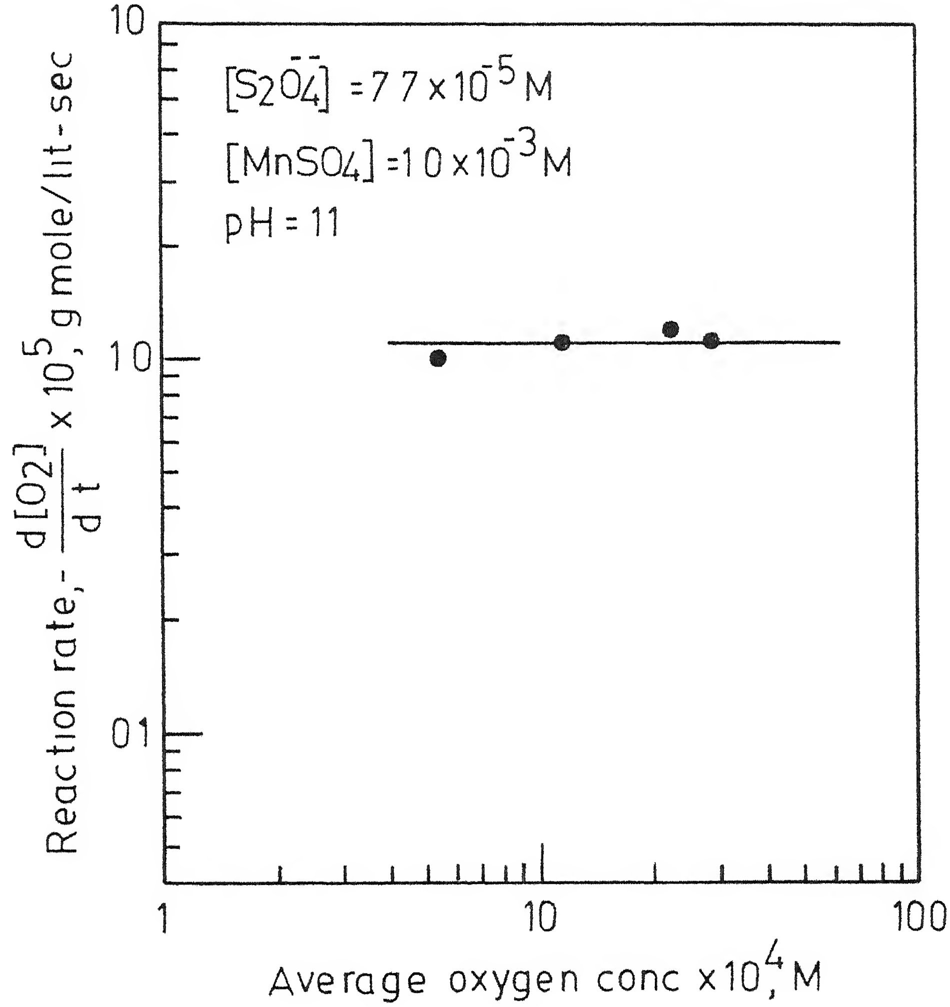

Fig 13 - Effect of oxygen concentration in presence of $MnSO_4$ at 30°C

concentration varied in the range of 3.8×10^{-5} to 1.2×10^{-2} M. The logarithmic of rate versus logarithmic of average dithionite concentration has been plotted in Figure 14. The slope of line indicated the first order variation of rate with respect of dithionite concentration.

4.3 Inhibition with Triethanolamine

Triethanolamine can be used to inhibit the dithionite oxidation reaction since it has been known to posses [9] a solvation capacity, a high affinity of the ion to sodium dithionite, and a reducing capacity.

Experimental data are presented in Tables 24 to 29, Appendix E. Reaction temperature was constant at 30°C.

4.3.1 Effect of Triethanolamine Concentration

The effect of triethanolamine concentration on the rate of dithionite oxidation was studied at a pH of 8. The concentrations of dithionite and oxygen solutions were kept constant as 7.7×10^{-5} and 1.2×10^{-3} M, respectively. Tables 24 and 25, Appendix E show all measured and calculated values. Triethanolamine concentration varied from 1.0×10^{-4} to 1.0×10^{-2} M.

Figure 15 shows the results of these experiments (Table 16). The apparent order of the reaction with respect to triethanolamine inhibitor was found to be 0.2, in constras

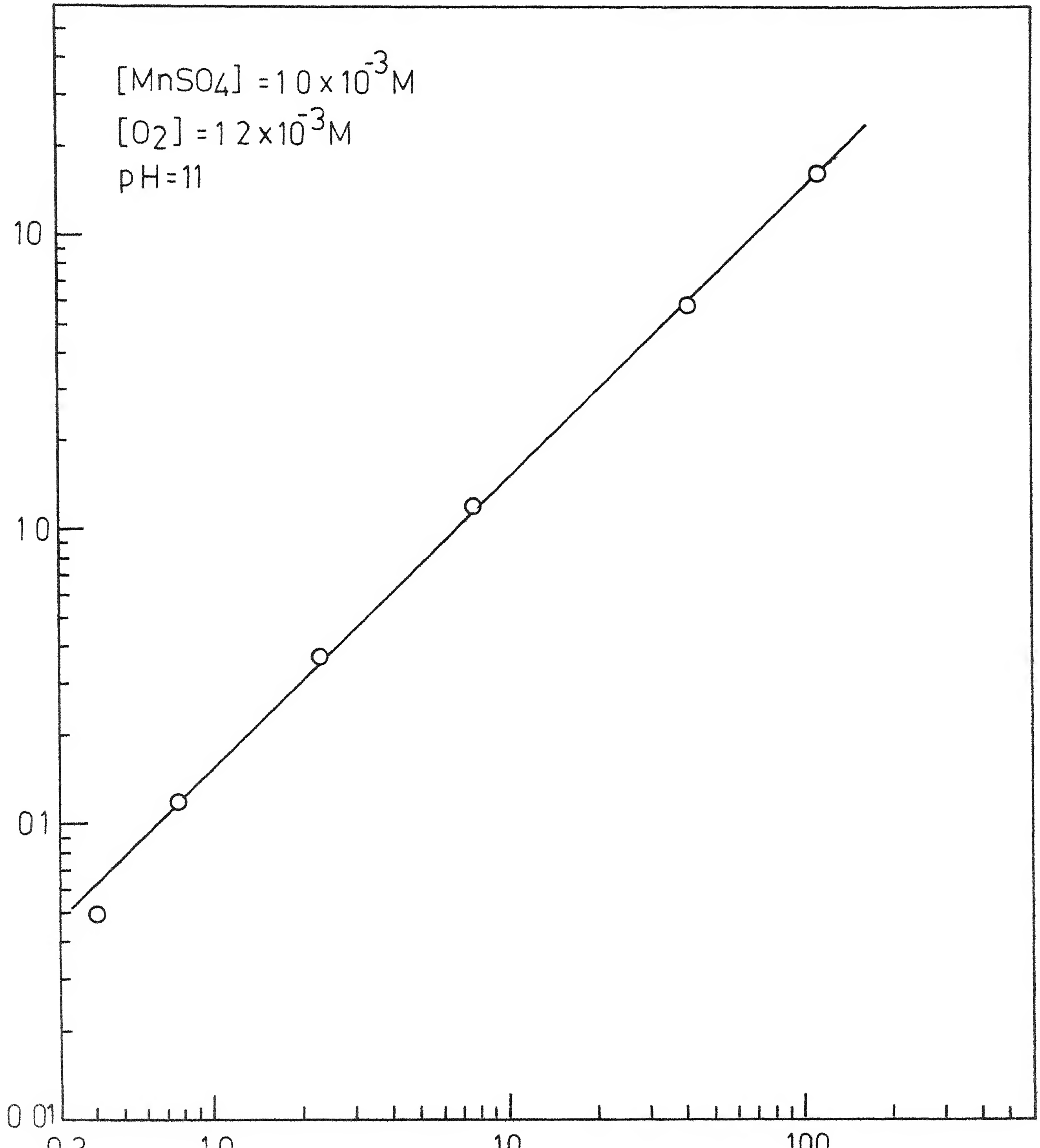

Fig 14 - Effect of dithionite on reaction rate in presence of $MnSO_4$ at 30 °C

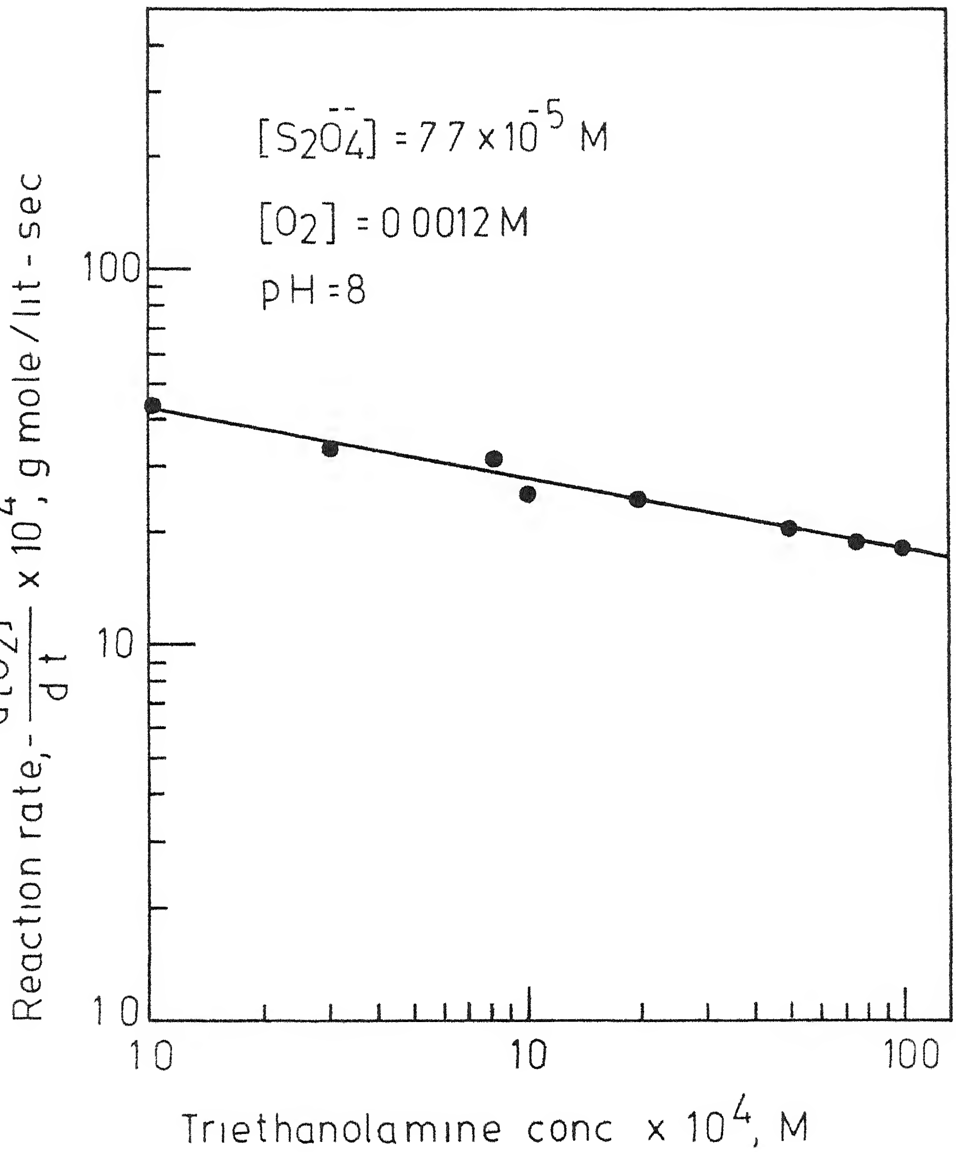

Fig 15 - Effect of triethanolamine concentration on reaction rate at 30°C

to the value of Mn based inhibitors.

4.3.2 Effect of Reactant Concentrations

These experiments are performed under the identical conditions as in 4.1 and 4.2 except inhibitor triethanolamine was used in place of $MnCl_2$ and $MnSO_4$. Data have been presented in Tables 26-29, Appendix E. Results are plotted in Figures 16 and 17. Again there were zero order and first order dependences of oxygen and dithionite, respectively.

The rate constants and standard deviations were calculated for each set of experiments. The results are summarized in Table 2. An examination of the standard deviations show that the uncertainty is very low.

For comparison, the results of the uninhibited and inhibited runs are shown in Figure 18. It is seen that under identical conditions of pH, temperature and reactant concentrations, the inhibiting effects of $MnCl_2$ and $MnSO_4$ were comparatively higher than that of triethanolamine. The rate reduced two times in the presence of triethanolamine and eight times with manganese salts.

There appears to be no data available on inhibition, and therefore, it limits the discussion on these results. However, based on these findings a reaction mechanism has been proposed, as described in the next chapter.

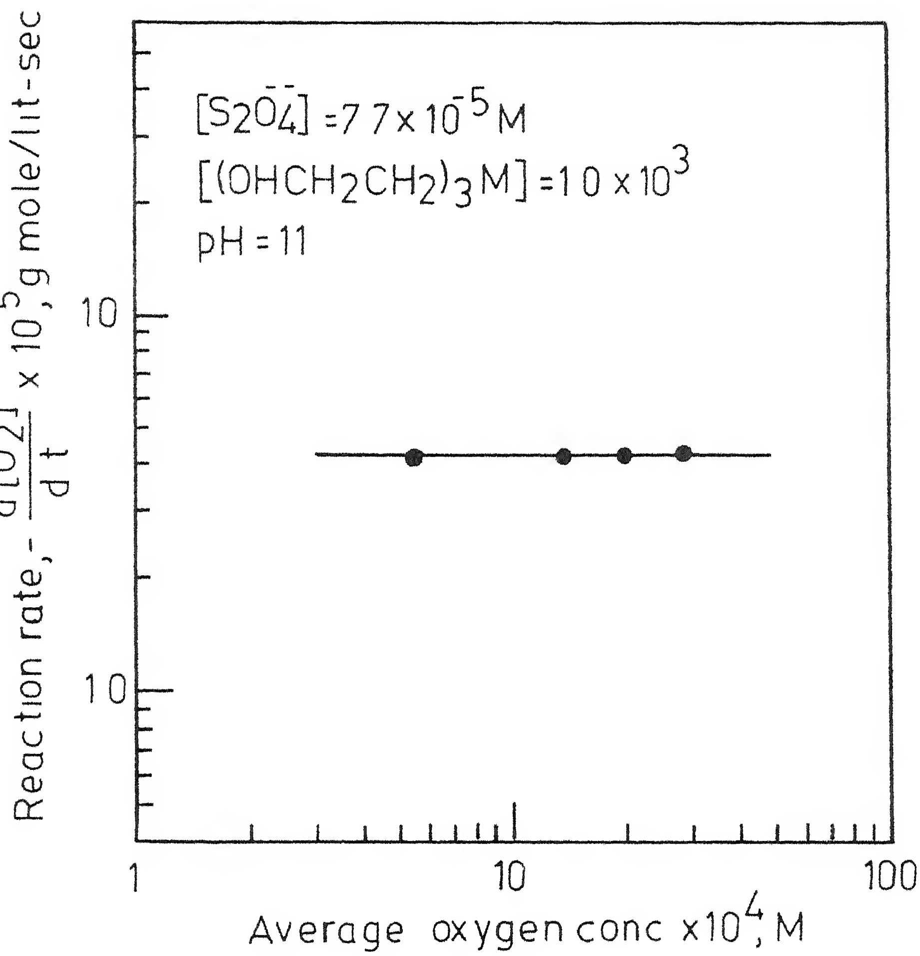

Fig 16 - Effect of oxygen on reaction rate in presence of triethanolamine at 30°C

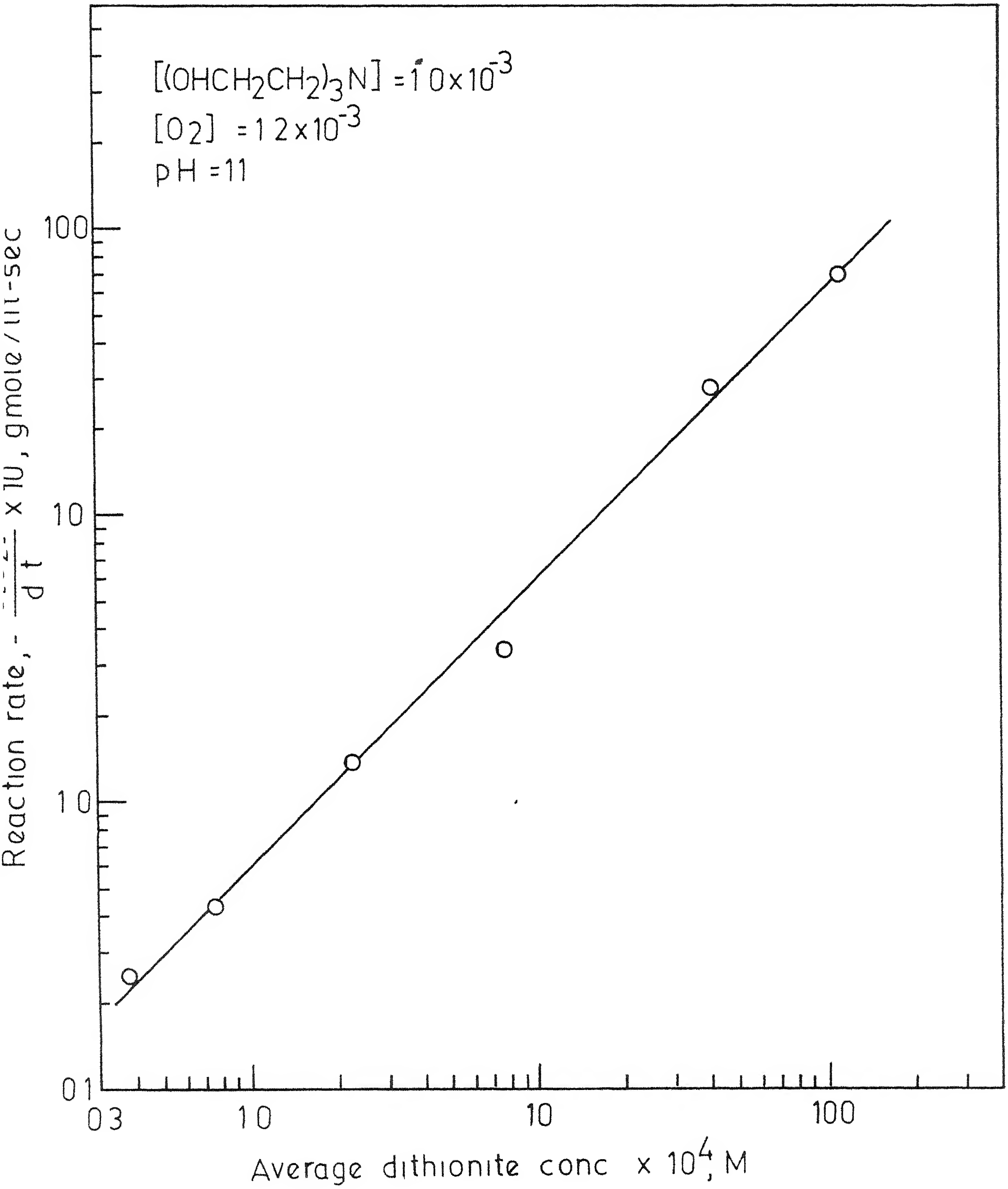

Fig 17 - Effect of dithionite on reaction rate in presence of triethanolamine at 30°C

TABLE 2: RATE CONSTANTS AND STANDARD DEVIATIONS

Runs[δ]	Rate Constants	Standard Deviations
CI ($MnCl_2$)	4.3×10^{-2} $M^{0.8}$ Sec^{-1}	3.1×10^{-3}
OI ($MnCl_2$)	6.7×10^{-4} $M^{0.8}$ Sec^{-1}	4.3×10^{-6}
DI ($MnCl_2$)	6.8×10^{-4} $M^{0.8}$ Sec^{-1}	3.1×10^{-5}
SI ($MnSO_4$)	2.0×10^{-2} $M^{0.9}$ Sec^{-1}	1.4×10^{-4}
OS ($MnSO_4$)	3.2×10^{-4} $M^{0.9}$ Sec^{-1}	2.4×10^{-5}
DS ($MnSO_4$)	3.2×10^{-4} $M^{0.9}$ Sec^{-1}	2.4×10^{-5}
TI[$(OHCH_2CH_2)_3N$]	1.2×10^{1} $M^{0.2}$ Sec^{-1}	7.5×10^{-1}
OT[$(OHCH_2CH_2)_3N$]	1.8×10^{-1} $M^{0.2}$ Sec^{-1}	9.3×10^{-4}
DT[$(OHCH_2CH_2)_3N$]	2.0×10^{-1} $M^{0.2}$ Sec^{-1}	2.5×10^{-2}

[δ] CI, OI, DI, etc are the runs designated for various set of experiments (see nomenclature)

CHAPTER 5

REACTION MECHANISM

The complexity of sodium dithionite oxidation reaction and its senstivity to inhibition suggest that it proceeds by radical chains. A mechanism which satisfies established order of reaction with respect to dithionite and oxygen and in which the initial step was dissociation of dithionite to produce a free radical, is given as

1. $S_2O_4^{--} \xrightarrow{k_1} 2\dot{S}O_2^-$

2. $\dot{S}O_2^- + O_2 \xrightarrow{k_2} \dot{S}O_4^-$

3. $\dot{S}O_4^- + H_2O \xrightarrow{k_3} HSO_4^- + \dot{O}H$

4. $S_2O_4^{--} + \dot{O}H \xrightarrow{k_4} HSO_3^- + \dot{S}O_2^-$

5. $\dot{S}O_4^- + \dot{O}H^- \xrightarrow{k_5}$ Inactive product

The above steps represent a typical chain reaction.

5.1 Derivation of Rate Expression-Uninhibited

The reaction (1) is an initiation step in which $\dot{S}O_2^-$ produced acts as active centers [4,5,47]. Then the propagation step (2) produces another active center, $\dot{S}O_4^-$. The sulfate ion radicals react with water to form HSO_4^-. The $\dot{O}H$ radical produced in step (3) reacts with dithionite to

produce HSO_3^- ions as shown by step (4). These steps have ample precedence in the literature [45, 48, 49]. Since the rate of reaction is independent of oxygen concentration, the oxygen addition step is the most rapid step and therefore, does not limit the overall rate. In aqueous medium the probability of water influencing the overall rate seems to be remote, thus excluding step (3) as the controlling step. So the active center $\dot{SO}_2^-$ is present in low concentration as compared to $\dot{OH}$ and $\dot{SO}_4^-$. It may, therefore, be assumed that the active centers $\dot{SO}_4^-$ and $\dot{OH}$ are rate limiting. In the present scheme, obviously, the significant termination step is reaction (5).

The rate of oxygen consumption is given by the rate determining step (4) which is written as

$$-\frac{d[O_2]}{dt} = k_4\ [S_2O_4^{--}]\ [\dot{OH}] \qquad (5.1)$$

To derive the final rate expression following equations can be written,

$$\frac{d[\dot{SO}_2^-]}{dt} = k_1\ [S_2O_4^{--}] - k_2[\dot{SO}_2^-]\ [O_2] + k_3\ [S_2O_4^{--}]\ [\dot{OH}] \qquad (5.2)$$

$$\frac{d[\dot{SO}_4^-]}{dt} = k_2[\dot{SO}_2^-]\ [O_2] - k_3[\dot{SO}_4^-]\ [H_2O] - k_5\ [\dot{SO}_4^-]\ [\dot{OH}] \qquad (5.3)$$

$$\frac{d[\underset{\bullet}{OH}]}{dt} = k_3[\underset{\bullet}{SO_4^-}]\,[H_2O] - k_4\,[S_2O_4^{--}]\,[\underset{\bullet}{OH}] + k_5\,[\underset{\bullet}{SO_4^-}]\,[\underset{\bullet}{OH}] \qquad (5.4)$$

Assuming that steady state concentrations exist for $\underset{\bullet}{SO_2^-}$, $\underset{\bullet}{SO_4^-}$ and $\underset{\bullet}{OH}$ radicals, left hand side of Equations 5.2, 5.3 and 5.4 equal to zero. Following concentrations can be derived

$$[\underset{\bullet}{SO_2^-}] = \frac{[S_2O_4^{--}]\,(k_1 + k_4[\underset{\bullet}{OH}])}{k_2[O_2]} \qquad (5.5)$$

$$[\underset{\bullet}{SO_4^-}] = \frac{k_2\,[\underset{\bullet}{SO_2^-}]\,[O_2]}{k_3\,[H_2O] + k_5[\underset{\bullet}{OH}]} \qquad (5.6)$$

$$[\underset{\bullet}{OH}] = \frac{k_3[\underset{\bullet}{SO_4^-}]\,[H_2O]}{k_4[S_2O_4^{--}] + k_5[\underset{\bullet}{SO_4^-}]} \qquad (5.7)$$

Substitution of $[\underset{\bullet}{SO_2^-}]$ from Equation 5.5 in Equation 5.6 gives

$$[\underset{\bullet}{SO_4^-}] = \frac{[S_2O_4^{--}](k_1 + k_4[\underset{\bullet}{OH}])}{k_3[H_2O] + k_5[\underset{\bullet}{OH}]} \qquad (5.8)$$

The expression for $[\underset{\bullet}{OH}]$ is obtained after eliminating $[\underset{\bullet}{SO_4^-}]$ from Equations 5.7 and 5.8

$$[\underset{\bullet}{OH}] = \frac{k_3}{k_5}\,[H_2O] \qquad (5.9)$$

The square of the concentration of radical $[\underset{\bullet}{OH}]$ has been neglected since the radical concentration itself is very low. Substituting $[\underset{\bullet}{OH}]$ from Equation 5.9 in

Equation 5.1 we obtain

$$-\frac{d[O_2]}{dt} = \frac{k_4 k_3}{k_5} [H_2O] [S_2O_4^{--}] \tag{5.10}$$

whence,

$$-\frac{d[O_2]}{dt} = K_A [S_2O_4^{--}] \tag{5.11}$$

where $$K_A = \frac{k_3 k_4}{k_5} [H_2O] \tag{5.12}$$

The rate expression 5.11 is consistent with the experimental orders for uninhibited dithionite oxidation reaction.

5.2 Derivation of Rate Expressions - Inhibited:

The inhibiting effect of $MnCl_2$, $MnSO_4$ and triethanolamine may be attributed to the direct termination and/or deactivation of active radicals, for example, the transfer reaction between radicals and inhibitors or the formation of an inactive complex by the inhibitors. Therefore, it is fair to assume that the chain termination proceeds according to

$$6. \quad \dot{S}O_4^- + [I] \xrightarrow{k_6} \text{Inactive Product},$$

since $\dot{S}O_4^-$ radical is present in high concentration. Indeed, this chain termination by the inhibitor is competitive with the reaction (5), but in the presence of

appreciable concentration of manganese salts, the former reaction will be predominant.

When the termination proceeds according to step (6), the following equations can be derived.

$$[\dot{SO}_2^-] = \frac{[S_2O_4^{--}]\ (k_1 + k_4\ [\dot{O}H]}{k_2[O_2]} \tag{5.5}$$

$$[\dot{SO}_4^-] = \frac{k_2\ [\dot{SO}_2^-]\ \ [O_2]}{k_3\ [H_2O] + k_6\ [I]} \tag{5.13}$$

$$[\dot{O}H] = \frac{k_3\ [\dot{SO}_4]\ \ [H_2O]}{k_4\ [S_2O_4^{--}]} \tag{5.14}$$

These derivations are based on the steady state hypothesis of intermediate radicals. Eliminating $[\dot{SO}_2^-]$ and $[\dot{SO}_4^-]$ from above equations one obtains

$$[\dot{O}H] = \frac{k_3k_1}{k_4k_5}\ \frac{[H_2O]}{[I]} \tag{5.15}$$

Substitution of $[\dot{O}H]$ in Equation 5.1 results the following rate expression

$$-\frac{d[O_2]}{dt} = \frac{k_3k_1}{k_5}\ [H_2O]\ \frac{[S_2O_4^{--}]}{[I]} \tag{5.16}$$

$$-\frac{d[O_2]}{dt} = K_B\ \frac{[S_2O_4^{--}]}{[I]} \tag{5.17}$$

where $$K_B = \frac{k_3k_1}{k_5}\ [H_2O] \tag{5.18}$$

When both the termination steps (5,6) are significant, one can derive the following equations

$$[\dot{SO}_2^-] = \frac{[S_2O_4^{--}]\ (k_1+k_4\ [\dot{O}H])}{k_2[O_2]} \tag{5.5}$$

$$[\dot{SO}_4^-] = \frac{k_2[\dot{SO}_2^-]\ [O_2]}{k_3[H_2O] + k_5[\dot{O}H] + k_6[I]} \tag{5.19}$$

$$[\dot{O}H] = \frac{k_3\ [\dot{SO}_4^-]\ [H_2O]}{k_4\ [S_2O_4^{--}] + k_5[\dot{SO}_4^-]} \tag{5.20}$$

Substitution of $[\dot{SO}_2^-]$ from Equation 5.5 in Equation 5.19 gives

$$[\dot{SO}_4^-] = \frac{[S_2O_4^{--}]\ (k_i+k_4[\dot{O}H])}{k_3[H_2O] + k_5[\dot{O}H] + k_6[I]} \tag{5.21}$$

solution of Equations 5.20 and 5.21 gives

$$[\dot{O}H] = \frac{k_i k_3\ [H_2O]}{k_5 k_1 + k_4 k_6\ [I]} \tag{5.22}$$

It is fair to assume that $k_4k_6[I] << k_5k_1$ since k_4 is the rate constant for the rate determining step and [I] is in extremely low concentrations. Therefore,

$$[\dot{O}H] = \frac{k_3}{k_5}\ [H_2O] \tag{5.23}$$

$$-\frac{d[O_2]}{dt} = \frac{k_3k_4}{k_5}\ [H_2O]\ [S_2O_4^{--}] \tag{5.24}$$

or $$\frac{-d[O_2]}{dt} = K_C \; [S_2O_4^{--}] \tag{5.25}$$

where $$K_C = \frac{k_3 k_4}{k_5} \; [H_2O] \tag{5.26}$$

If the chain termination is assumed to be reaction (6), then the corresponding rate expression is Equation 5.16 which is in good agreement with the experimental results for $MnCl_2$ and $MnSO_4$ inhibitors. From the figures 9 and 12 it can be concluded that concentration of $MnCl_2$ and $MnSO_4$ inhibitors are inversely proportional to the total concentrations of $MnCl_2$ or $MnSO_4$ present in the reaction solution.

When the chain termination proceeds according to steps (5) and (6), the derived rate expression 5.24 satisfies the experimental findings of triethanolamine-inhibited runs.

5.3 Comparison Between Observed and Predicted Rates

All the three rate expressions 5.11 , 5.17 , and 5.25 derived from the proposed mechanism were subjected to the error analyses, using least square estimation techniques. The rate constants predicted from these rate expressions together with those obtained experimentally are given in Table 3. Four typical plots of the calculate

TABLE 3: COMPARISON BETWEEN OBSERVED AND PREDICTED RATE CONSTANTS

Experiments[α]	$K_{observed}$	$K_{predicted}$	Standard Deviation
RD (uninhibited)	1.32	1.32	1.4×10^{-1}
RO (uninhibited)	1.30	1.30	8.7×10^{-2}
CI ($MnCl_2$ Runs)	4.3×10^{-2}	7.2×10^{-3}	3.5×10^{-3}
OI ($MnCl_2$ Runs)	6.7×10^{-4}	1.7×10^{-4}	1.1×10^{-6}
DI ($MnCl_2$ Runs)	6.8×10^{-4}	1.7×10^{-4}	7.9×10^{-6}
SI ($MnSO_4$) Runs)	2.0×10^{-2}	6.8×10^{-3}	1.9×10^{-3}
OS ($MnSO_4$ Runs)	3.2×10^{-4}	1.4×10^{-4}	1.1×10^{-5}
DS ($MnSO_4$ Runs)	3.2×10^{-4}	1.3×10^{-4}	8.0×10^{-6}
TI (Triethanolamine Runs)	1.2×10^{1}	3.4×10^{1}	1.0×10^{1}
OT (Triethanolamine Runs)	1.8×10^{-1}	5.5×10^{-1}	2.8×10^{-3}
DT (Triethanolamine Runs)	2.0×10^{-1}	6.0×10^{-1}	7.5×10^{-2}

[α]RD, RO, CI, are the runs designated for various set of experiments (see nomenclature)

rate versus observed rate for uninhibited, $MnCl_2$, $MnSO_4$ and triethanolamine inhibited runs are shown in Figures 19-22. The rates were calculated from Equation 5.17 for $MnCl_2$ and $MnSO_4$ and from Equation 5.25 for triethanolamine. For uninhibited, it was calculated from Equation 5.11 . The maximum deviation between the predicted values and the experimental ones have been found to be ± 10 per cent for all these cases. In the inhibited runs where the dependencies of inhibitor concentrations were studied, the standard deviations were larger than 10 per cent (Table 3).

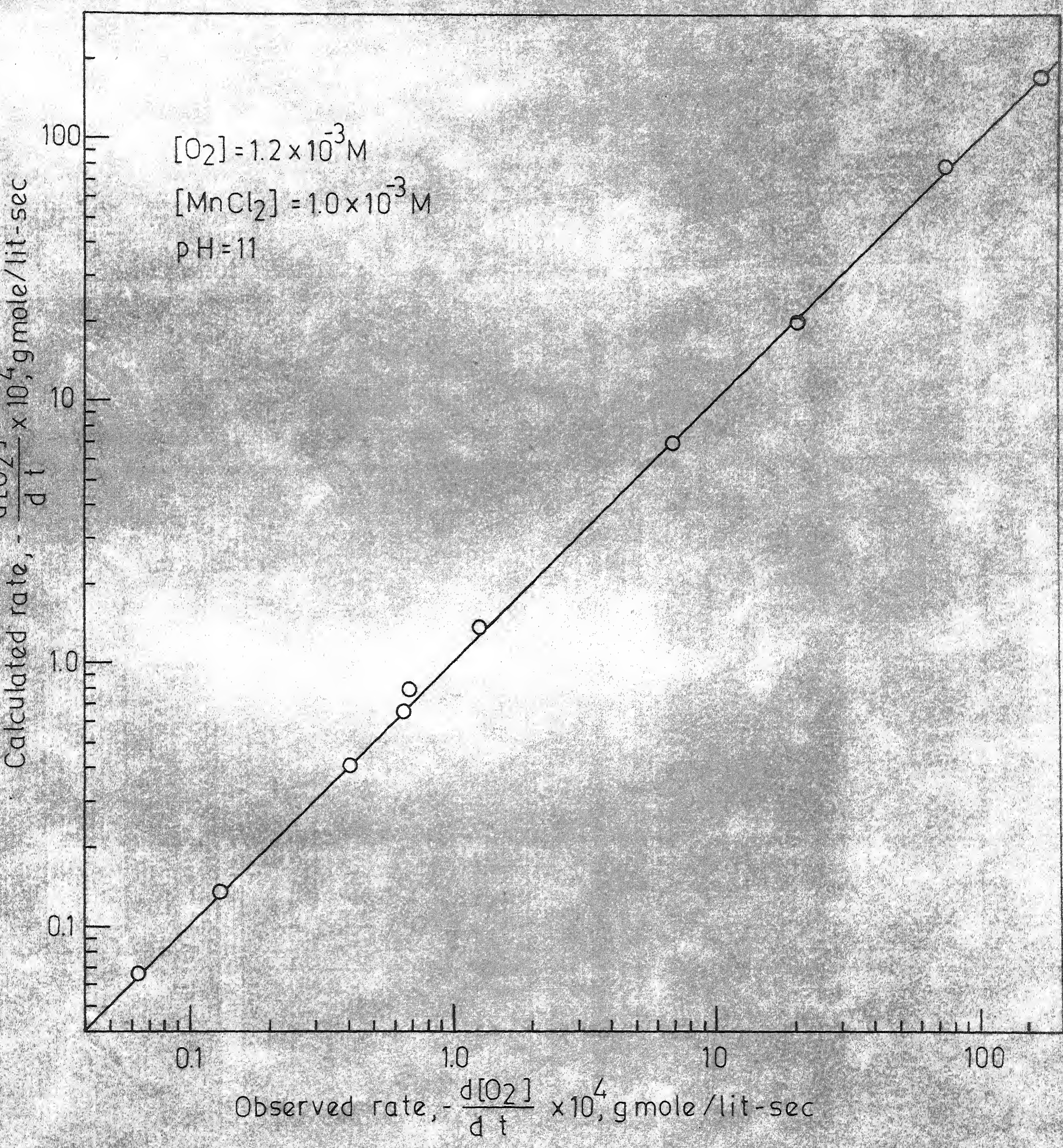

Fig. 19 - Comparison of observed and calculated rates of disappearance of oxygen; $MnCl_2$-inhibited runs.

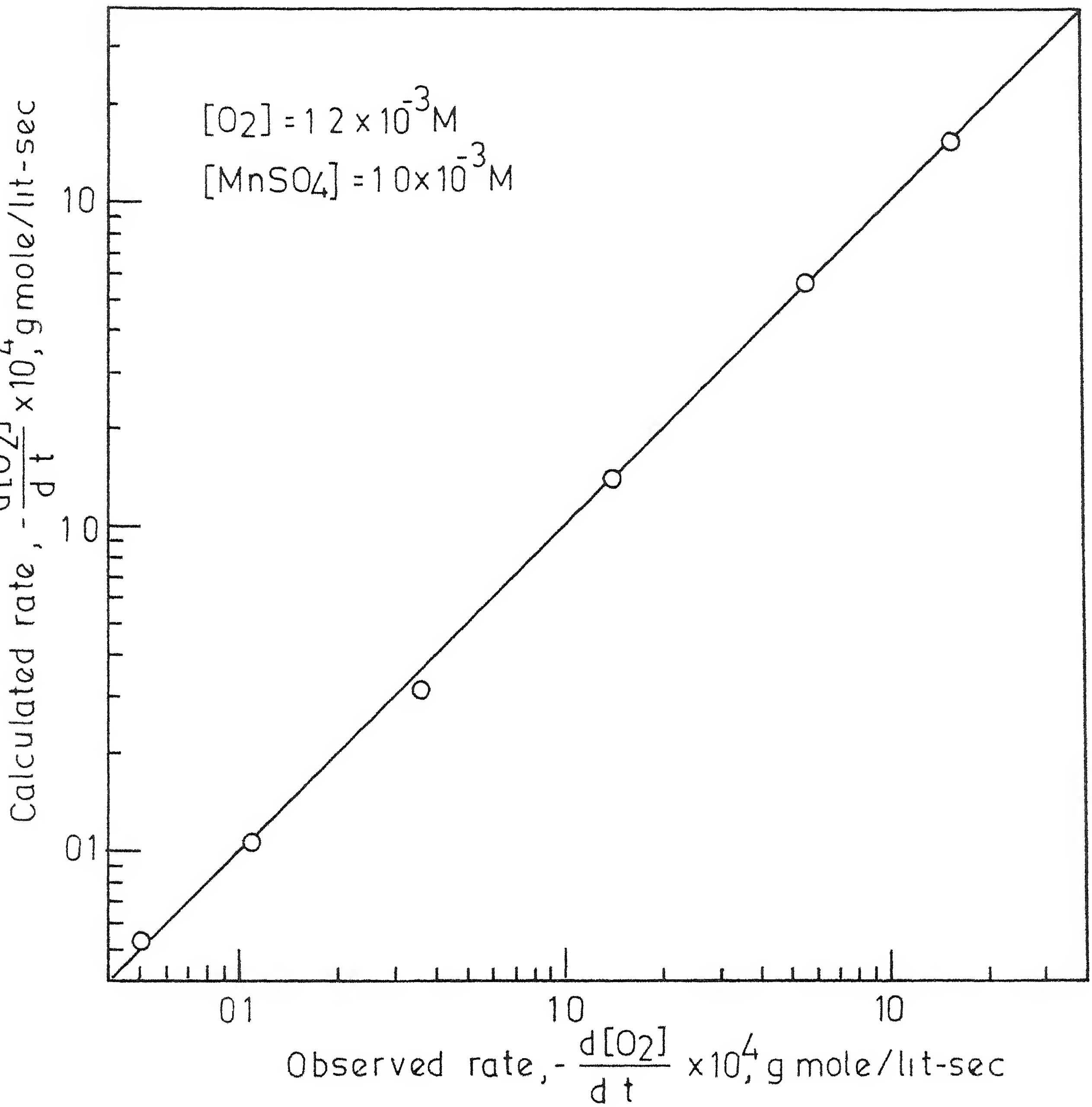

Fig 20 - Comparison of observed and calculated rates of disappea of oxygen, $MnSO_4$-inhibited runs

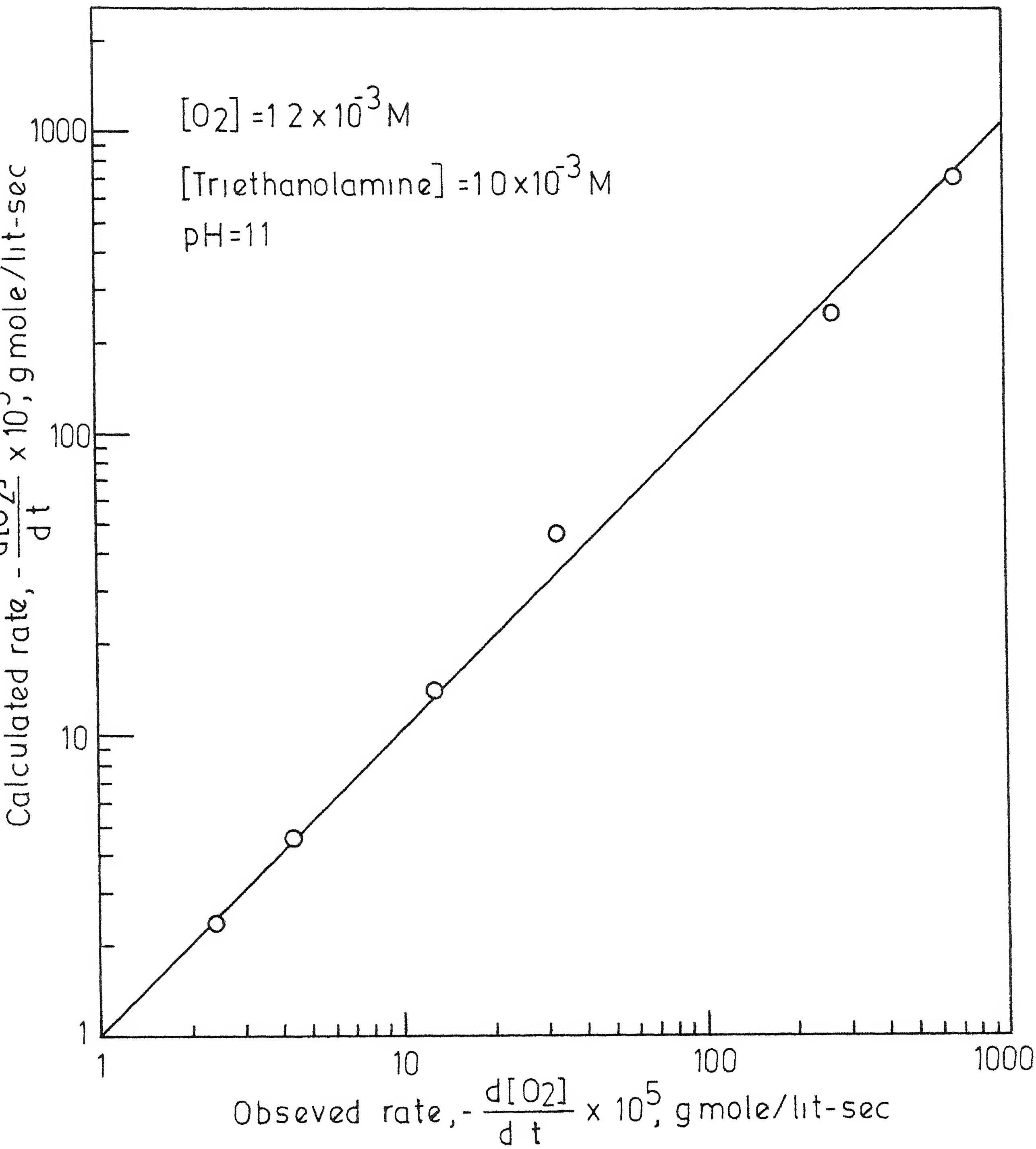

Fig 21 - Comparison of observed and calculated rate of disappeare of oxygen, triethanolamine-inhibited runs

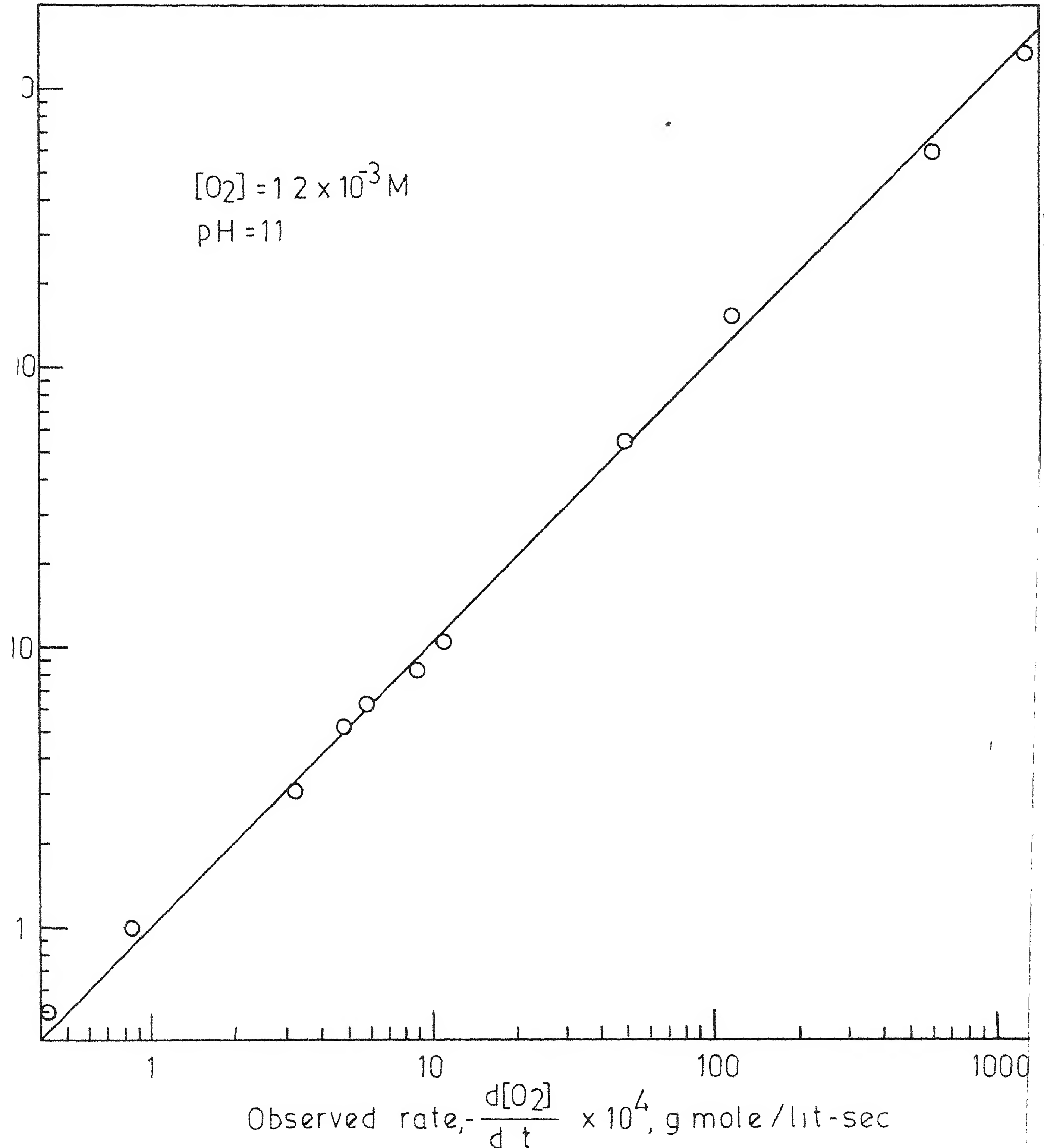

Fig 22 - Comparison of observed and calculated rates of disappearence of oxygen, uninhibited runs

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

The experimental data obtained from this study of kinetics of oxidation of sodium dithionite in the liquid phase have been compared with previously reported results. The data on the inhibited runs were presented for the first time. It is concluded that the most important contribution of this work was in setting up a mechanism and the rate expressions which satisfy the behaviour of the dithionite oxidation system with and without inhibitors.

Based on the experimental results of the present study as discussed in preceding chapters, the following conclusions are drawn.

6.1 Conclusions

6.1.1 Oxidation of Dithionite: Uninhibited Runs

Results on the oxidation study show that the reaction is first order with respect to dithionite and zero order with respect to molecular oxygen. The overall stoichiometry conforms to that reported in [3,4].

An activation energy of 17.5 Kcal/gmole has been calculated for this reaction.

Parametric dependence of pH of the reacting medium on the reaction rate has also been followed. It

has been observed that the rate decreases in a regular pattern with increase of pH. This has been attributed to the possibility of dithionite undergoing hydrolysis as a result of which the available dithionite concentration for oxidation is reduced.

6.1.2 Oxidation of Dithionite: Inhibited Runs

Rate data have been obtained for the oxidation of sodium dithionite inhibited with $MnCl_2$, $MnSO_4$ and triethanolamine. In all cases the dependencies on oxygen and dithionite resulted in zero and one power relation respectively. The reaction rate was found to be 0.2 order with respect to triethanolamine, 0.8 order with respect to $MnCl_2$ and 0.9 order with respect to $MnSO_4$.

6.1.3 Reaction Mechanism

The following free radical chain mechanism has been proposed:

$$S_2O_4^{--} \xrightarrow{k_1} 2\dot{S}O_2^-$$

$$\dot{S}O_2^- + O_2 \xrightarrow{k_2} \dot{S}O_4^-$$

$$\dot{S}O_4^- + H_2O \xrightarrow{k_3} HSO_4^- + \dot{O}H$$

$$S_2O_4^{--} + \dot{O}H \xrightarrow{k_4} HSO_3^- + \dot{S}O_2^-$$

$$\dot{S}O_4^- + \dot{O}H \xrightarrow{k_5} \text{In active product}$$

$$\dot{S}O_4^- + [I] \xrightarrow{k_6} \text{Inactive product.}$$

which on steady state analysis give rise to following rate expressions:

$$-\frac{d[O_2]}{dt} = K_A\,[S_2O_4^{--}] \quad \text{Termination by step (5)} \tag{5.11}$$

$$-\frac{d[O_2]}{dt} = K_B\,\frac{[S_2O_4^{--}]}{[I]} \quad \text{Termination by step (6)} \tag{5.17}$$

$$\frac{-d\,[O_2]}{dt} = K_C\,[S_2O_4^{--}] \quad \text{Termination by steps (5) and (6)} \tag{5.25}$$

These rate expressions (5.11), (5.17) and (5.25) satisfactorily accounted the kinetic data observed for uninhibited, $MnCl_2$ and $MnSO_4$ inhibited and triethanolamine inhibited runs, respectively.

It is expected that the present results would contribute to the understanding of kinetics and mechanism of this reaction.

6.2 Recommendations

6.2.1 Modification of the Equipment

The capacity of the pressurized storage tanks should be increased to allow for longer runs. In this way, the steady state temperature could be more readily and accurately determined.

6.2.2 Recommendations for Further Studies

Valuable informations might be obtained for this system from study of the intermediates, such as those proposed in the above reaction mechanism.

Kinetics of some rapid reactions should also be studied by this technique.

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APPENDIX A

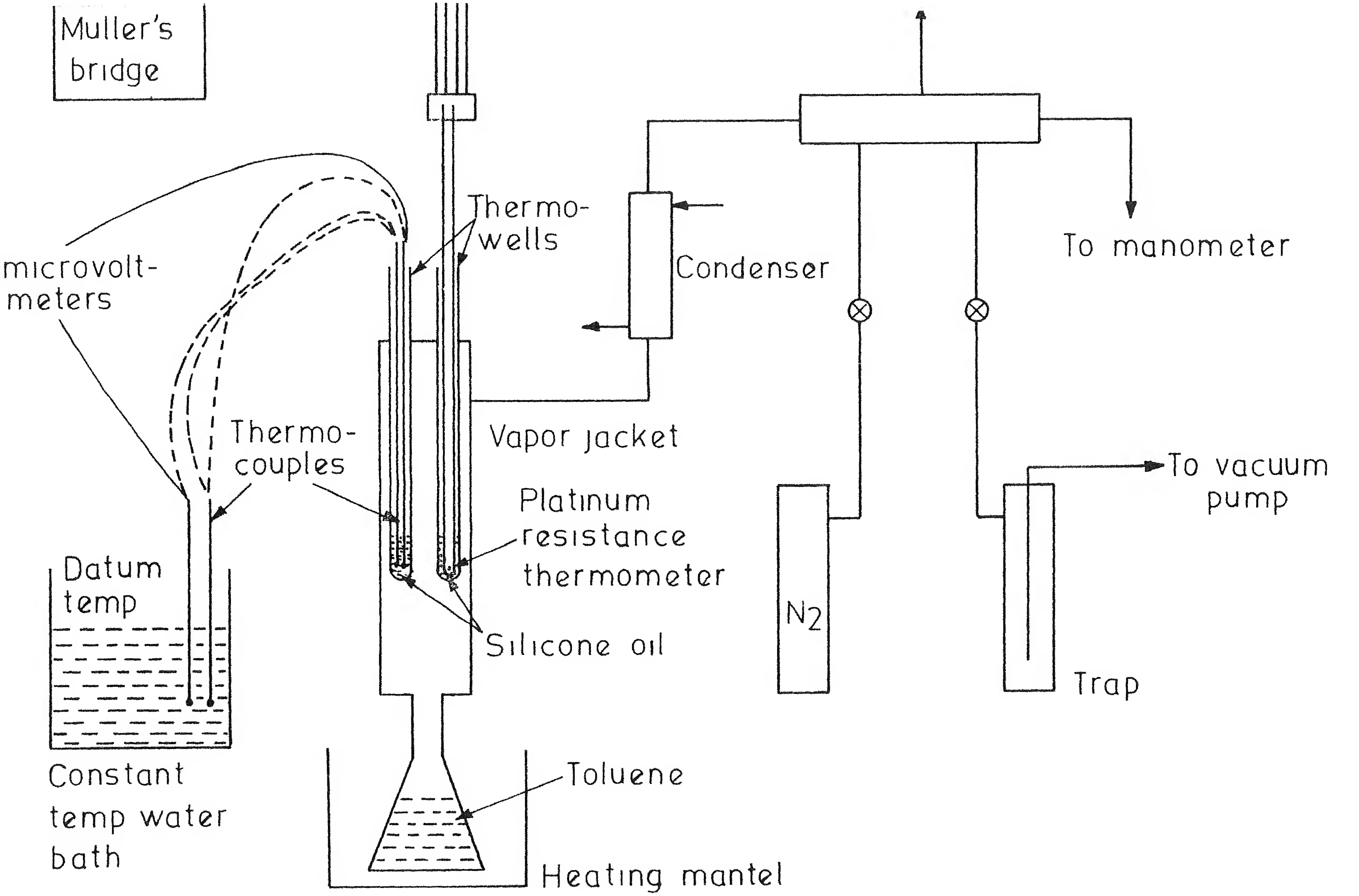
CALIBRATION OF THERMOCOUPLES

CALIBRATION OF THERMOCOUPLES

Thermocouples were made and calibrated against a 25 ohm Leeds and Northrup platinum resistance thermometer and Muller bridge assembly. The details of the apparatus and procedure are given below.

Apparatus

The apparatus is shown schematically in Figure 23. The principal part of the apparatus is the vapor jacket. If the flask attached to the bottom of the vapor jacket, a pure liquid is taken and boiled at a constant total pressure in an inert atmosphere of nitrogen. The vapors will condense in the condenser and are recirculated back to the flask. The principle behind this is due to the fact that a vapor substance boils at a constant temperature when the total pressure is fixed. In order to dampen the pressure fluctuations, thereby temperature fluctuations, the volume of the system was increased by connecting two 20 liter flasks (ballasts) to the system. The temperature inside the vapor can be varied by changing the nitrogen pressure in the system. Changes in the nitrogen pressure can be affected by the vacuum pump and high pressure nitrogen cylinder with a low pressure regulator connected



23 - Schematic diagram of the experimental set-up for calibration of the thermocouples

to the system. The vapor jacket has a glass at its top which carries two thermowells in the vapor jacket.

Procedure

The platinum resistance thermometer was inserted into one of the thermowells. Since the platinum resistance thermometer was calibrated by the U.S. National Bureau of Standards with seven centimeter depth of immersion, same depth was kept under silicone oil in the thermowell. One set of differential thermocouples which was used in the observation tube was placed into the other thermowell while the other set of thermocouples which was used at the mixing point was kept in the constant temperature water bath, the temperature of which was kept constant at the datam temperature by the thermostat. A desired volume of toluene was charged to the flask attached to the bottom of the vapor jacket. The system was then evacuated and left at this stage for an hour to check if there was any leakage. Finally, the system was filled by nitrogen to the required pressure. The heating mantel was turned on and toluene started boiling after some time. The steady value of the resistance of the platinum resistance thermometer was measured using Muller bridge and the corresponding output voltage was measured directly on

the microvoltmeter. These measurements were repeated at various nitrogen pressures in the system. The pressures were so chosen that the temperature inside the vapor jacket, as measured by the platinum resistance thermometer, was always higher than the datum temperature of the constant temperature water bath and the temperature difference was of the order of 0 to 15^{o}C.

The resistance of the platinum resistance thermometer bears a certain relationship with the temperature surrounding the element of the platinum resistance thermometer. The resistance temperature relationship for the platinum resistance thermometer is described by Cellender's equation. The values of the constants of this equation are supplied along with the thermometer. Using this equation and the given constants, a table is generated with the help of computer to give the values of temperatures at different resistance values of the platinum resistance thermometer. This table was used to read directly the temperature from the resistance of platinum resistance thermometer. Figure 24 is the plot of the data recorded for thermocouples at datum temperature of 30^{o}C. Using the L.M.S. curve fit the following relation was obtained

$$(\text{Output})_{mV} = 0.6366 \times (\text{Temperature Difference, } ^{o}\text{C})$$

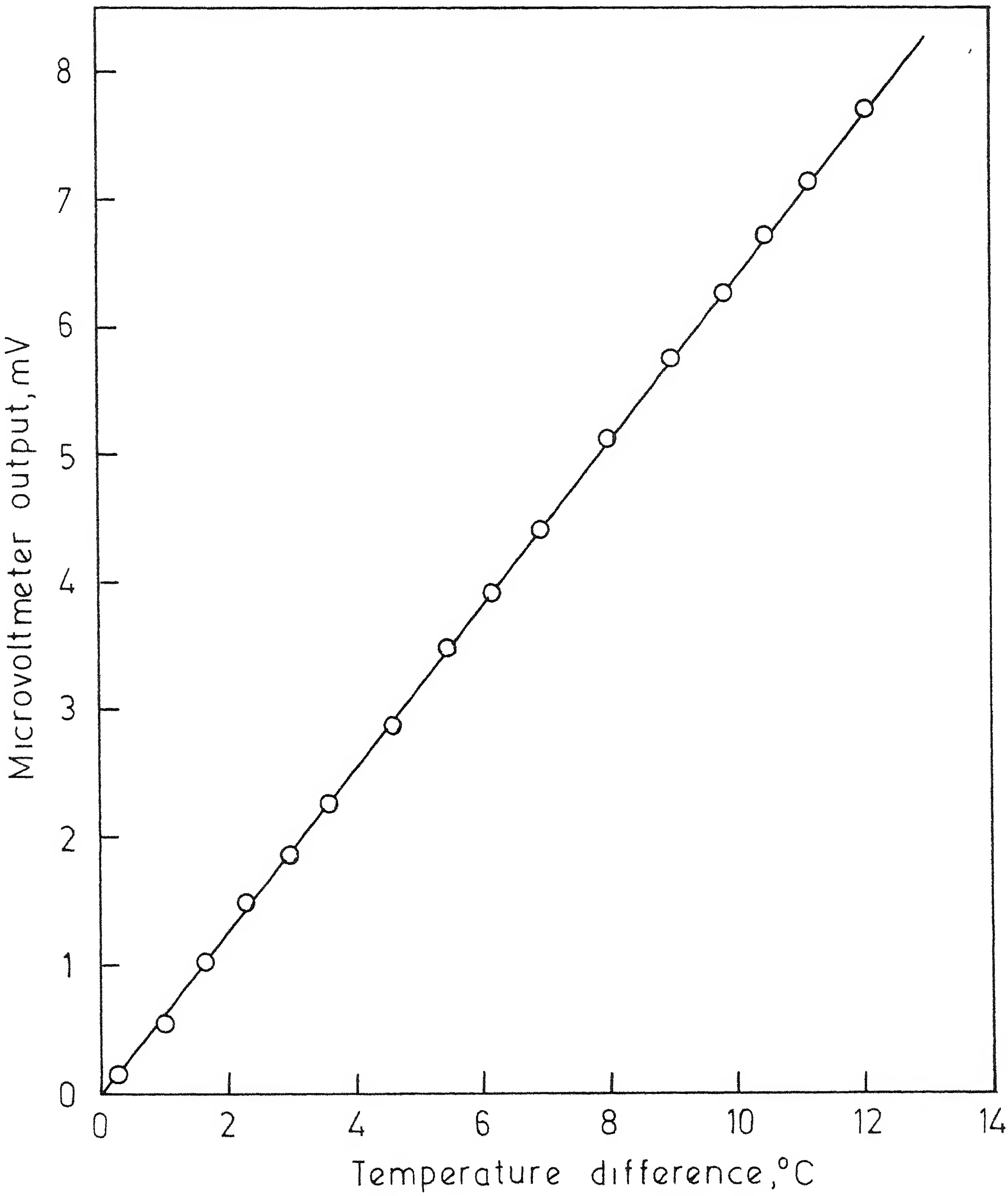


Fig 24 - Calibration curve for thermocouples at 30°C

APPENDIX B

DATA FOR OXIDATION OF SODIUM DITHIONITE - UNINHIBITED RUNS

TABLE 4: RECORDED DATA FOR UNINHIBITED O_2-SODIUM DITHIONITE SYSTEM EFFECT OF pH

Reaction Temperature = 30°C

pH	Stock Solution: Concn. of Dithionite (M)	Stock Solution: Concn of Oxygen (M)	Volume of the Reactor (cm^3)	Flow Rate of Dithionite Solution (ml/sec)	Flow Rate of Oxygen Solution (ml/sec)	Microvoltmeter output (mV)
2	3	4	5	6	7	8
8	0.0005	0.0013	0.16	2.3745	28.50	0.00166
			0.16	1.8996	22.80	0.00204
			0.16	1.5830	19.00	0.00248
			0.16	1.4247	17.10	0.00270
			0.16	1.2564	15.20	0.00309
			0.16	1.1081	13.30	0.00315
			0.16	0.9498	11.40	0.00315
9	0.005	0.00128	0.16	0.7916	9.50	0.00086
			0.16	0.4777	6.33	0.00137
			0.16	0.3166	3.80	0.00220
			0.16	0.1583	1.90	0.00318
			2.53	1.5830	19.00	0.00318

(contd)

2	3	4	5	6	7	8
10	0.0005	0.00125	0.16	1.5830	19.00	0.00016
			0.16	0.7916	9.50	0.00016
			0.16	0.4777	6.33	0.00016
			2.53	1.5830	19.00	0.00073
			2.53	0.7916	9.50	0.00143
			2.53	0.4777	6.33	0.00207
			5.02	0.7916	9.50	0.00277
			5.02	0.6332	7.60	0.00318
			5.02	0.4777	6.33	0.00318
8	0.001	0.00126	0.16	2.3745	28.50	0.00236
			0.16	1.5830	19.00	0.00251
			0.16	1.1872	14.25	0.00471
			0.16	1.1081	13.30	0.00507
			0.16	0.7916	9.50	0.06366
			0.16	0.6332	7.60	0.06366
9	0.001	0.00135	0.16	1.5830	19.00	0.00057
			0.16	0.7916	9.50	0.00108
			0.16	0.4777	6.33	0.00146

Table 4 (contd)

1	2	3	4	5	6	7	8
				0.16	0.3166	3.80	0.00261
				0.16	0.1583	1.90	0.00535
				2.53	1.5830	19.00	0.00700
				2.53	1.4247	17.10	0.00700
RP-6	10	0.001	0.00125	0.16	0.7916	9.50	0.00019
				0.16	0.4777	6.33	0.00032
				2.53	1.5830	19.00	0.00159
				2.53	0.7916	9.50	0.00312
				2.53	0.4777	6.33	0.00446
				5.02	0.7916	9.50	0.00592
				5.02	0.6332	7.60	0.06366
				14.43	1.5830	19.00	0.06366
RP-7	8	0.005	0.00129	0.16	2.3745	28.50	0.01496
				0.16	1.5830	19.00	0.02234
				0.16	1.2564	15.20	0.02763
				0.16	1.1872	14.25	0.02865
				0.16	1.1081	13.30	0.03183

Table 4 (contd)

1	2	3	4	5	6	7	8
				0.16	0.9498	11.40	0.03183
				0.16	0.7916	9.5	0.03183
RP-8	9	0.005	0.00131	0.16	1.5830	19.00	0.00316
				0.16	0.7916	9.50	0.00541
				0.16	0.4777	6.33	0.00955
				0.16	0.3166	3.80	0.01592
				0.16	0.1583	1.90	0.02871
				2.53	1.5830	19.00	0.03183
				2.53	1.4247	17.10	0.03183
RP-9	10	0.005	0.0013	0.16	0.7916	9.50	0.00159
				0.16	0.4777	6.33	0.00159
				2.53	1.5003	19.00	0.00955
				2.53	0.7916	9.50	0.01910
				2.53	0.4777	6.33	0.02865
				5.02	0.7916	9.50	0.03119
				5.02	0.6332	7.60	0.03119
RP-10	8	0.010	0.00135	0.16	2.3745	28.50	0.03297
				0.16	1.5830	19.00	0.04902

1	2	3	4	5	6	7	8
				0.16	1.2564	15.20	0.06110
				0.16	0.9498	11.40	0.06366
				0.16	0.7916	9.50	0.06366
RP-11	9	0.010	0.0013	0.16	1.5830	19.00	0.00637
				0.16	0.7916	9.50	0.01237
				0.16	0.4777	6.33	0.01846
				0.16	0.1583	1.90	0.06175
				2.53	1.5830	19.00	0.06175
				2.53	1.4247	17.10	0.06175
RP-12	10	0.010	0.0013	0.16	0.7916	9.50	0.00138
				0.16	0.4777	6.33	0.00138
				2.53	1.5830	19.00	0.02228
				2.53	0.7916	9.50	0.04456
				2.53	0.4777	6.33	0.06366
				5.02	0.7916	9.50	0.06366

TABLE 5: CALCULATED DATA FOR UNINHIBITED O_2-SODIUM DITHIONITE SYSTEM

EFFECT OF pH

Reaction Temperature = 30°C

Run No.	pH	In Reactor: Average Dithionite Solution (M)	In Reactor: Average Oxygen Solution (M)	Total Flow Rate (ml/sec)	Residence Time (Sec)	Rise in Temperature (°C)	Reaction Rate (M/sec)
1	2	3	4	5	6	7	8
RP-1	8	3.85×10^{-5}	0.0012	30.8745	0.00517	0.0026	3.75×10^{-3}
				24.6996	0.00646	0.0032	
				20.5830	0.00775	0.0039	
				18.4247	0.00861	0.00425	
				16.4564	0.00969	0.00485	
				14.4081	0.01107	0.00495	
				12.3498	0.01292	0.00495	
RP-2	9	3.85×10^{-5}	0.0012	10.2916	0.01550	0.00135	2.7×10^{-4}
				6.8107	0.02342	0.00215	
				4.1166	0.03875	0.00345	
				2.0583	0.07745	0.005	
				20.5830	0.12292	0.005	

Table 5 (contd)

1	2	3	4	5	6	7	8
RP-3	10	3.85×10^{-5}	0.0012	20.5830	0.00775	0.00025	7.4×10^{-5}
				10.2916	0.0155	0.00025	
				6.8107	0.02342	0.00025	
				20.583	0.12292	0.00115	
				10.2916	0.24583	0.00225	
				6.8107	0.37151	0.00325	
				11.2916	0.4878	0.00435	
				8.2332	0.60973	0.005	
				6.8107	0.738	0.005	
RP-4	8	7.72×10^{-5}	0.0012	30.8745	0.00517	0.0037	5.33×10^{-3}
				20.5830	0.00775	0.0055	
				15.4372	0.01033	0.0074	
				14.4081	0.01107	0.0079	
				10.2916	0.01550	0.0100	
				8.2332	0.01937	0.0100	
RP-5	9	7.72×10^{-5}	0.0012	20.			

Table 5 (contd)

1	2	3	4	5	6	7	8
RP-5	9	7.72×10^{-5}	0.0012	20.5830	0.00775	0.0009	7.9×10^{-4}
				10.2916	0.0155	0.0017	
				6.8107	0.02342	0.0023	
				4.1166	0.03875	0.0041	
				2.0583	0.07745	0.0084	
				20.5830	0.12292	0.0110	
				18.5247	0.13665	0.0110	
RP-6	10	7.72×10^{-5}	0.0012	10.2916	0.01550	0.0003	1.4×10^{-4}
				6.8107	0.02342	0.0005	
				20.5830	0.12292	0.0025	
				10.2916	0.24583	0.0049	
				6.8107	0.37151	0.0070	
				10.2916	0.48778	0.0093	
				8.2332	0.60973	0.0100	
				20.5830	0.70106	0.0100	
RP-7	8	38.5×10^{-5}	0.0012	30.8745	0.00517	0.0235	3.4×10^{-2}
				20.5830	0.00775	0.0351	
				16.4564	0.00969	0.0454	

Table 5 (contd)

1	2	3	4	5	6	7	8
				15.4372	0.01033	0.045	
				14.4081	0.01107	0.050	
				12.3498	0.01292	0.050	
				10.2916	0.01550	0.050	
RP-8	9	38.5×10^{-5}	0.0012	20.5830	0.00775	0.0050	4.3×10^{-3}
				10.2916	0.0155	0.0085	
				6.8107	0.02342	0.0150	
				4.1166	0.03875	0.025	
				2.0583	0.07745	0.0451	
				20.583	0.12292	0.050	
				18.5247	0.13665	0.050	
RP-9	10	38.5×10^{-5}	0.0012	10.2916	0.0155	0.0025	9.07×10^{-4}
				6.8107	0.02342	0.0025	
				20.5830	0.12292	0.0150	
				10.2916	0.24583	0.0300	
				6.8107	0.37151	0.0450	
				10.2916	0.48778	0.049	
				8.2332	0.609	0.049	

TABLE 6: RECORDED DATA FOR UNINHIBITED O_2-SODIUM DITHIONITE SYSTEM

EFFECT OF OXYGEN CONCENTRATION

Reaction Temperature = $30^{o}C$
pH = 11

Run No.	Stock Solution: Conc. of Dithionite (M)	Stock Solution: Conc. of Oxygen (M)	Volume of the Reactor (cm^3)	Flow Rate of the Dithionite Solution (ml/sec)	Flow Rate of the Oxygen Solution (μl/sec)	Microvoltmeter output (mV)
1	2	3	4	5	6	7
RO-1	0.0005	0.000586	0.16	0.7916	9.500	0.00005
			0.16	0.5277	6.330	0.00079
			2.53	1.5833	19.000	0.00341
			2.53	0.7916	9.500	0.00784
			2.53	0.5277	6.330	0.00108
			5.02	0.7916	9.550	0.00134
			14.43	1.5833	19.000	0.00210
			5.02	0.5277	6.330	0.00229
RO-2	0.0005	0.00124	0.16	0.7916	9.500	0.00004
			0.16	0.5277	6.330	0.00064
			2.53	1.5833	19.00	0.00037
			2.53	0.7916	9.50	0.00071
			2.53	0.5277	6.33	0.00115

Table 6 (contd)

1	2	3	4	5	6	7
			5.02	0.7916	9.50	0.00127
			14.43	1.5833	19.00	0.00210
			5.02	0.5277	6.33	0.00220
RO-3	0.0005	0.0024	0.16	0.7916	9.50	0.00004
			0.16	0.5277	6.33	0.00074
			2.53	1.5833	19.00	0.00034
			2.53	0.7916	9.50	0.00070
			2.53	0.5277	6.33	0.00107
			5.02	0.7916	9.50	0.00134
			14.43	1.5833	19.00	0.00223
			5.02	0.5277	6.33	0.00225
RO-4	0.0005	0.00315	0.16	0.7916	9.50	0.00004
			0.16	0.5277	6.33	0.00019
			2.53	1.5833	19.00	0.00038
			2.53	0.7916	9.50	0.00072
			2.53	0.5277	6.33	0.00107
			5.02	0.7916	9.50	0.00131

Table 6 (contd)

1	2	3	4	5	6	7
			14.43	1.5833	19.00	0.00196
			5.02	0.5277	6.33	0.00254
RO-5	0.01	0.000583	0.16	0.7916	9.50	0.00095
			0.16	0.5277	6.33	0.00127
			2.53	1.5833	19.00	0.00955
			2.53	0.7916	9.50	0.01910
			2.53	0.5277	6.33	0.02865
			5.02	0.7916	9.50	0.03438
			14.43	1.5833	19.00	0.03514
RO-6	0.01	0.00124	2.53	1.5833	19.00	0.00957
			2.53	0.7916	9.50	0.01910
			2.53	0.5277	6.33	0.02960
			5.02	0.7916	9.50	0.03469
RO-7	0.01	0.0024	0.16	0.7916	9.50	0.00127
			0.16	0.5277	6.33	0.00350
			2.53	1.5833	19.00	0.01019
			2.53	0.7916	9.50	0.01908
			2.53	0.5277	6.33	0.02865

Table 6 (contd)

1	2	3	4	5	6	7
RO-8	0.01	0.00315	0.16	0.7916	9.50	0.00331
			0.16	0.5277	6.33	0.00127
			2.53	1.5833	19.00	0.00987
			2.53	0.7916	9.50	0.01910
			2.53	0.5277	6.33	0.03119
			5.02	0.7916	9.50	0.03660
RO-9	0.15	0.00124	0.16	1.18725	14.25	0.01019
			0.16	0.7916	9.50	0.01592
			0.16	0.4749	5.70	0.02610
			0.16	0.3166	3.80	0.03883
			0.16	0.1583	1.90	0.07958
RO-10	0.15	0.0024	0.16	1.18725	14.25	0.01273
			0.16	0.4749	5.70	0.02801
			0.16	0.3166	3.80	0.04074
			0.16	0.1583	1.90	0.08021
			2.53	1.5830	19.00	0.12732
RO-11	0.15	0.00315	0.16	0.4777	6.33	0.02546
			0.16	0.1583	1.90	0.08276
			2.53	1.5830	19.00	0.12732

1	2	3	4	5	6	7
			2.53	1.2564	15.20	0.15278
			2.53	0.9498	11.40	0.20690
RO-12	1.3	0.00124	0.16	2.3745	28.50	0.05729
			0.16	1.18996	22.80	0.07130
			0.16	1.5830	19.00	0.08658
			0.16	1.4247	17.10	0.09549
RO-13	1.3	0.0024	0.16	2.3745	28.50	0.05729
			0.16	1.5830	19.00	0.08658
			0.16	1.2564	15.20	0.10950
			0.16	1.1081	13.30	0.13241
RO-14	1.3	0.00315	0.16	1.5830	19.00	0.08725
			0.16	1.4247	17.10	0.09867
			0.16	1.18725	14.25	0.11459
			0.16	0.7916	9.50	0.17500
			0.16	0.6332	7.60	0.21963

TABLE 7: CALCULATED DATA FOR UNINHIBITED O_2-SODIUM DITHIONITE SYSTEM
EFFECT OF OXYGEN CONCENTRATION

Reaction Temperature = 30°C
pH = 11

Run No.	In Reactor: Average Dithionite Conc. (M)	In Reactor: Average Oxygen Conc. (M)	Total Flow Rate (ml/sec)	Residence Time (sec)	Rise in Temperature (°C)	Reaction Rate (M/sec)
RO-1	3.85×10^{-5}	5.42×10^{-4}	10.2916	0.0154	0.00008	4.64×10^{-5}
			6.8160	0.0235	0.00012	
			20.5830	0.1230	0.00054	
			10.2916	0.2460	0.00120	
			6.8160	0.3680	0.00171	
			10.2916	0.4380	0.00209	
			20.5830	0.6950	0.00332	
			6.8160	0.7380	0.00361	
RO-2	3.85×10^{-5}	1.15×10^{-3}	10.2916	0.0154	0.00006	4.64×10^{-5}
			6.8160	0.0235	0.00011	
			20.5830	0.1230	0.00064	
			10.2916	0.2460	0.00112	
			6.8160	0.3680	0.00180	
			10.2916	0.4380	0.00231	

Table 7 (contd)

1	2	3	4	5	6	7
			20.5830	0.6950	0.00333	
			6.8160	0.7380	0.00350	
RO-3	3.85×10^{-5}	2.22×10^{-3}	10.2916	0.0154	0.00006	4.58×10^{-5}
			6.8160	0.0235	0.00012	
			20.5830	0.1230	0.00060	
			10.2916	0.2460	0.00111	
			6.8160	0.3680	0.00172	
			10.2916	0.4380	0.00209	
			20.5830	0.6950	0.00350	
			6.8160	0.7380	0.0035	
RO-4	3.85×10^{-5}	2.92×10^{-3}	10.2916	0.0154	0.00006	4.58×10^{-5}
			6.8160	0.0235	0.00033	
			20.5830	0.1230	0.00061	
			10.2916	0.2460	0.00114	
			6.8160	0.3680	0.00169	
			10.2916	0.4380	0.00206	
			20.5830	0.6950	0.00308	
			6.8160	0.7380	0.00411	

Table 7 (contd)

1	2	3	4	5	6	7
RO-5	7.71×10^{-4}	5.41×10^{-4}	10.2916	0.0154	0.0015	9.0×10^{-4}
			6.8160	0.0235	0.00201	
			20.5830	0.1230	0.01514	
			10.2916	0.2460	0.03002	
			6.8160	0.3680	0.0450	
			10.2916	0.4380	0.0540	
			20.5830	0.6950	0.05521	
RO-6	7.7×10^{-4}	1.15×10^{-3}	20.5830	0.1230	0.01510	9.3×10^{-4}
			10.2916	0.2460	0.03011	
			6.8160	0.3680	0.04651	
			10.2916	0.4380	0.05450	
RO-7	7.71×10^{-3}	2.22×10^{-3}	10.2916	0.0154	0.00201	9.0×10^{-4}
			6.8160	0.0235	0.00550	
			20.5830	0.1230	0.01610	
			10.2916	0.2460	0.03000	
			6.8160	0.3680	0.04400	
			10.2916	0.4380	0.05350	
RO-8	7.7×10^{-3}	2.92×10^{-3}	10.2916	0.0154	0.0025	9.7×10^{-4}

Table 7 (contd)

1	2	3	4	5	6	7
			20.5830	0.1230	0.0155	
			10.2916	0.2460	0.03112	
			6.8160	0.3680	0.0491	
			10.2916	0.4380	0.0575	
RO-9	$1.15x10^{-2}$	$1.15x10^{-3}$	15.4372	0.01033	0.0160	$1.21x10^{-2}$
			10.2916	0.0155	0.0250	
			6.1749	0.02583	0.0410	
			4.1166	0.03875	0.0610	
			2.0583	0.07745	0.1250	
RO-10	$1.15x10^{-2}$	$2.22x10^{-3}$	15.4372	0.01033	0.0210	$1.21x10^{-2}$
			6.1749	0.02583	0.0440	
			4.1166	0.03875	0.0640	
			2.0583	0.07745	0.1260	
			20.5830	0.12292	0.2000	
RO-11	$1.15x10^{-2}$	$2.92x10^{-3}$	6.8107	0.02342	0.0410	$1.20x10^{-2}$
			2.0583	0.07745	0.1320	
			20.5830	0.1229	0.2020	
			16.4664	0.15374	0.2430	

Table 7 (contd)

1	2	3	4	5	6	7
RO-12	1.00×10^{-1}	1.15×10^{-3}	30.8745	0.00517	0.0910	1.3×10^{-1}
			24.6996	0.00646	0.1120	
			1.5830	0.00775	0.1360	
			18.4247	0.00861	0.1490	
RO-13	1.00×10^{-1}	2.22×10^{-3}	30.8745	0.00517	0.0900	1.32×10^{-1}
			1.5830	0.00775	0.1360	
			16.4564	0.00969	0.1720	
			14.4081	0.01107	0.2080	
RO-14	1.001×10^{-1}	2.92×10^{-3}	20.5830	0.00775	0.1300	1.3×10^{-1}
			18.4287	0.00861	0.1550	
			15.43725	0.01033	0.1800	
			10.2916	0.01550	0.2750	
			8.2332	0.01937	0.3450	

TABLE 8: RECORDED DATA FOR UNINHIBITED O_2-SODIUM DITHIONITE SYSTEM

EFFECT OF DITHIONITE CONCENTRATION

Reaction Temperature = $30^{\circ}C$
pH = 11

Run No.	Stock Solution: Conc. of Dithionite (M)	Stock Solution: Conc. of Oxygen (M)	Volume of the Reactor (cm^3)	Flow Rate of Dithionite Solution (ml/sec)	Flow Rate of Oxygen Solution (ml/sec)	Microvoltmeter Output (mV)
1	2	3	4	5	6	7
RD-1	0.0005	0.0013	0.16	0.7916	9.500	0.00005
			0.16	0.5277	6.330	0.00009
			2.53	1.5839	19.000	0.00043
			2.53	0.7916	9.500	0.00088
			2.53	0.5277	6.330	0.00132
			5.02	0.7916	9.500	0.00158
			14.43	1.5833	19.000	0.00253
			5.02	0.5277	6.330	0.00261
			5.02	0.4749	5.700	0.00268
			14.43	1.1872	14.250	0.00318
			14.43	1.1081	13.300	0.00318
RD-2	0.0010	0.00139	0.16	0.7916	9.50	0.00010
			0.16	0.5277	6.33	0.00019
			2.53	1.5833	19.[illegible]	0.00089

Table 8 (contd)

1	2	3	4	5	6	7
			2.53	0.7916	9.50	0.00175
			2.53	0.5277	6.33	0.00267
			5.02	0.7916	9.50	0.00321
			5.02	0.6332	7.60	0.00439
			14.43	1.5833	19.00	0.00484
			5.02	0.5277	6.33	0.00541
			14.43	1.1872	14.25	0.00633
			5.02	0.3166	3.80	0.00633
			14.43	0.7916	9.50	0.00633
RD-3	0.0030	0.00140	0.16	0.7916	9.50	0.00032
			0.16	0.5277	6.33	0.00064
			2.53	1.5833	19.00	0.00344
			2.53	0.7916	9.50	0.00764
			2.53	0.5277	6.33	0.01019
			5.02	0.7916	9.50	0.01273
			5.02	0.6332	7.60	0.01782

Table 8 (contd)

1	2	3	4	5	6	7
			14.43	1.5833	19.00	0.01901
			5.02	0.5277	6.33	0.01901
RD-4	0.0050	0.00130	0.16	0.7916	9.50	0.00064
			0.16	0.5277	6.33	0.00127
			2.53	1.5833	19.00	0.00509
			2.53	0.7916	9.50	0.01050
			2.53	0.5277	6.33	0.01496
			5.02	0.7916	9.50	0.01751
			5.02	0.6332	7.60	0.02542
			14.43	1.5833	19.00	0.02928
			5.02	0.4749	5.70	0.03183
			14.43	1.1872	14.25	0.03183
RD-5	0.0060	0.0015	0.16	0.7916	9.50	0.00064
			0.16	0.5277	6.33	0.00127
			2.53	1.5833	19.00	0.00640
			2.53	0.7916	9.50	0.01273
			2.53	0.5277	19.00	0.01910
			5.02	0.7916	9.50	0.02292

Table 8 (contd)

1	2	3	4	5	6	7
			14.43	1.5833	19.00	0.03563
			5.02	0.4749	5.70	0.03883
			14.43	1.1081	13.30	0.03883
			14.43	0.9498	11.40	0.03883
RD-6	0.0080	0.0016	0.16	0.7916	9.50	0.00127
			0.16	0.5277	6.33	0.00318
			2.53	1.5833	19.00	0.00923
			2.53	0.7916	9.50	0.01910
			2.53	0.5277	6.33	0.02769
			5.02	0.7916	9.50	0.03469
			5.02	0.6332	7.60	0.04775
			14.43	1.5833	19.00	0.05093
			5.02	0.4749	5.70	0.05284
RD-7	0.0100	0.0014	0.16	0.7916	9.50	0.00127
			0.16	0.5277	6.33	0.00191
			2.53	1.5833	19.00	0.01146
			2.53	0.7916	9.50	0.02324
			2.53	0.5277	6.33	0.03501

Table 8 (contd)

1	2	3	4	5	6	7
			5.02	0.7316	9.50	0.04138
			5.02	0.6332	7.60	0.05729
			14.43	1.5833	19.00	0.06366
			5.02	0.5277	6.33	0.06366
RD-8	0.0530	0.0013	0.16	0.4749	5.70	0.01082
			0.16	0.1583	1.90	0.03247
			2.53	1.5830	19.00	0.05156
			2.53	1.2564	15.20	0.07003
			2.53	1.1081	13.30	0.07383
RD-9	0.1510	0.0013	0.16	1.1872	14.25	0.01082
			0.16	0.6332	7.60	0.02101
			0.16	0.4777	6.33	0.02419
			0.16	0.3166	3.80	0.04074
RD-10	0.6020	0.0014	0.16	2.3745	28.50	0.03883
			0.16	1.1896	22.80	0.04838
			0.16	1.5830	19.00	0.05857
			0.16	1.2564	15.20	0.07257

Table 8 (contd)

1	2	3	4	5	6	7
RD-11	1.31	0.0013	0.16	2.3745	28.50	0.04011
			0.16	1.1896	22.80	0.05029
			0.16	1.5830	19.00	0.06048
			0.16	1.2564	15.20	0.07512

TABLE 9: CALCULATED DATA FOR UNINHIBITED O_2-SODIUM DITHIONITE SYSTEM

EFFECT OF DITHIONITE CONCENTRATION

Reaction Temperature = 30°C

pH = 11

Run No.	In Reactor: Average Dithionite concn. (M)	In Reactor: Average Oxygen Concn. (M)	Total Flow Rate (ml/sec)	Residence Time (sec)	Rise in Temperature (°C)	Reaction Rate (M/sec)
1	2	3	4	5	6	7
RD-1	3.85×10^{-5}	0.0012	10.2916	0.0154	0.00008	4.2×10^{-5}
			6.8160	0.0235	0.00014	
			20.5833	0.1230	0.00068	
			10.2916	0.2460	0.00138	
			6.8160	0.3680	0.00208	
			10.2916	0.4380	0.00248	
			20.5833	0.6950	0.00398	
			6.8160	0.7380	0.00412	
			6.1749	0.8130	0.00421	
			15.4372	0.9348	0.00500	
			14.4081	1.0015	0.00500	
RD-2	7.72×10^{-5}	0.0013	10.2916	0.0154	0.00015	8.6×10^{-5}
			6.8160	0.0235	0.00030	

Table 9 (contd)

1	2	3	4	5	6	7
			20.5833	0.1230	0.00140	
			10.2916	0.2460	0.00275	
			6.8160	0.3680	0.00420	
			10.2916	0.4380	0.00505	
			8.2332	0.6090	0.00690	
			20.5833	0.6950	0.00760	
			6.8160	0.7380	0.00850	
			15.4372	0.9347	0.01000	
			4.1166	1.2194	0.01000	
			10.2916	1.4020	0.01000	
RD-3	23.17×10^{-5}	0.0013	10.2916	0.0154	0.00050	3.27×10^{-4}
			6.8160	0.0235	0.00100	
			20.5833	0.1230	0.00540	
			10.2916	0.2460	0.01200	
			6.8160	0.3680	0.01600	
			10.2916	0.4380	0.02000	
			8.2332	0.6090	0.02800	
			20.5833	0.6950	0.03000	

Table 9 (contd)

1	2	3	4	5	6	7
RD-4	38.57×10^{-5}	0.0012	10.2916	0.0154	0.0010	4.81×10^{-4}
			6.8160	0.0235	0.0020	
			20.5833	0.1230	0.0080	
			10.2916	0.2460	0.0165	
			6.8160	0.3680	0.0235	
			10.2916	0.4380	0.0275	
			8.2332	0.6090	0.0400	
			20.5833	0.6950	0.0460	
			6.1749	0.8129	0.0500	
			15.4372	0.9347	0.0500	
RD-5	46.28×10^{-5}	0.0014	10.2916	0.0154	0.0010	5.98×10^{-4}
			6.8160	0.0235	0.0020	
			20.5833	0.1230	0.0100	
			10.2916	0.2460	0.0200	
			6.8160	0.3680	0.0300	
			10.2916	0.4380	0.0360	
			8.2332	0.6090	0.0490	
			20.5833	0.6950	0.0560	

Table 9 (contd)

1	2	3	4	5	6	7
			14.4081	1.0015	0.0600	
			12.3498	1.16844	0.0610	
RD-6	61.66×10^{-5}	0.0015	10.2916	0.0154	0.0020	9.07×10^{-4}
			6.8160	0.0235	0.0050	
			20.5833	0.1230	0.0145	
			10.2916	0.2460	0.0300	
			6.8160	0.3680	0.0435	
			10.2916	0.4380	0.0545	
			8.2332	0.6090	0.0750	
			20.5833	0.6950	0.0830	
			6.1749	0.8129	0.0830	
RD-7	77.8×10^{-5}	0.0013	10.2916	0.0154	0.0020	10.95×10^{-4}
			6.8160	0.0235	0.0030	
			20.5833	0.1230	0.0180	
			10.2916	0.2460	0.0365	
			6.8160	0.3680	0.0550	
			10.2916	0.4380	0.0650	
			8.2332	0.6090	0.0900	

Table 9 (contd)

1	2	3	4	5	6	7
RD-8	4.08×10^{-3}	0.0012	6.1749	0.02583	0.0170	4.91×10^{-3}
			2.0583	0.07745	0.0510	
			20.5830	0.12292	0.0813	
			16.4664	0.15374	0.1109	
			14.4081	0.17560	0.1163	
RD-9	1.16×10^{-2}	0.0012	15.4372	0.01033	0.0170	12.22×10^{-3}
			8.2332	0.01937	0.0332	
			6.8107	0.02342	0.0381	
			4.1166	0.03875	0.0642	
RD-10	4.64×10^{-2}	0.0014	30.8745	0.00517	0.0612	6.44×10^{-2}
			24.6996	0.00646	0.0761	
			20.5830	0.00775	0.0919	
			16.4564	0.00969	0.1141	
RD-11	1.00×10^{-1}	0.0012	30.8745	0.00517	0.0634	1.31×10^{-1}
			24.6996	0.00646	0.0793	
			20.5830	0.00775	0.0950	
			16.4564	0.00969	0.1182	

TABLE 10: RECORDED DATA FOR UNINHIBITED O_2-SODIUM DITHIONITE SYSTEM

EFFECT OF TEMPERATURE

$MnCl_2$ added in Dithionite solution $= 1.0 \times 10^{-3}$ M

$MnCl_2$ added in oxygen solution $= 1.0 \times 10^{-3}$ M

pH = 11

Run No.	Temperature (^oC)	Stock Solution: Conc. of Dithionite (M)	Stock Solution: Conc. of Oxygen (M)	Volume of the Reactor (cm^3)	Flow Rate of Dithionite solution (ml/sec)	Flow Rate of Oxygen Solution (ml/sec)	Microvoltmeter output (mV)
1	2	3	4	5	6	7	8
RT-1	30	0.001	0.0013	0.16	0.7916	9.50	0.00012
				0.16	0.5277	6.33	0.00019
				2.53	1.5833	19.00	0.00089
				2.53	0.7916	9.50	0.00175
				2.53	0.5277	6.33	0.00267
				5.02	0.7916	9.50	0.00321
				5.02	0.6332	7.60	0.00439
				14.42	1.1583	19.00	0.00484
				5.02	0.5277	6.33	0.00541
				14.43	1.1872	14.25	0.00633
				5.02	0.3166	3.80	0.00633
				14.43	0.7916	9.50	0.00633

Table 10(contd)

1	2	3	4	5	6	7	8
RT-2	45	0.001	0.0014	0.16	1.1872	14.25	0.00035
				0.16	0.7916	9.50	0.00051
				0.16	0.4777	6.33	0.00115
				0.16	0.3166	3.80	0.00150
				0.16	0.1583	1.90	0.00290
				2.53	1.5833	19.00	0.00462
RT-3	60	0.001	0.0014	0.16	1.2564	15.20	0.00059
				0.16	0.9498	11.40	0.00085
				0.16	0.4749	5.70	0.00179
				0.16	0.3166	3.80	0.00275
				0.16	0.1583	1.90	0.00465
RT-4	75	0.001	0.0012	0.16	1.5833	19.00	0.00259
				0.16	1.4247	17.10	0.00283
				0.16	1.2564	15.20	0.00325
				0.16	1.1872	14.25	0.00333
				0.16	0.9498	11.40	0.00427

Table 10 (contd)

1	2	3	4	5	6	7	8
RT-5	90	0.001	0.0013	0.16	2.3745	28.50	0.00471
				0.16	1.8996	22.80	0.00637
				0.16	1.5833	19.00	0.00637
				0.16	1.4297	17.10	0.00637
				0.16	1.2564	15.20	0.00637

TABLE 11: CALCULATED DATA FOR UNINHIBITED O_2-SODIUM DITHIONITE SYSTEM

EFFECT OF TEMPERATURE

Average $MnCl_2$ concentration in the Reactor = 1.0×10^{-3} M

pH = 11

Run No.	Temperature, (°C)	In Reactor: Average Dithionite conc. (M)	In Reactor: Average Oxygen concn. (M)	Total Flow Rate (ml/sec)	Residence Time (sec)	Temperature Rise (°C)	Reaction Rate (M/sec)
1	2	3	4	5	6	7	8
RT-1	30	7.72×10^{-5}	0.0012	10.2916	0.0154	0.00015	8.6×10^{-5}
				6.8160	0.0235	0.00030	
				20.5833	0.1230	0.00140	
				10.2916	0.2460	0.00275	
				6.8160	0.3680	0.00420	
				10.2916	0.4380	0.00505	
				6.2332	0.6 90	0.00690	
				20.5833	0.6950	0.00760	
				6.8160	0.7380	0.00850	
				15.4372	0.9347	0.01000	
				4.1166	1.2194	0.01000	
				10.2916	1.4020	0.01000	
RT-2	45	7.72×10^{-5}	0.0012	15.4372	0.0103	0.00055	4.379×10^{-4}

Table 11 (contd)

1	2	3	4	5	6	7	8
				6.8107	0.02342	0.00180	
				4.1166	0.03875	0.00235	
				2.0583	0.07745	0.00455	
				20.5833	0.12292	0.00725	
RT-3	60	7.72×10^{-5}	0.0013	16.4564	0.00969	0.00093	8.0×10^{-4}
				12.3498	0.01292	0.00134	
				6.1749	0.02583	0.00281	
				4.1166	0.03875	0.00432	
				2.0583	0.07745	0.00850	
RT-4	75	7.72×10^{-5}	0.0012	20.5833	0.00775	0.00404	3.926×10^{-3}
				18.4247	0.00861	0.00444	
				16.4564	0.00969	0.00511	
				15.4372	0.01033	0.00523	
				12.3498	0.01292	0.00670	
RT-5	90	7.72×10^{-5}	0.0012	30.8745	0.00517	0.00740	1.072×10^{-2}
				24.6996	0.00646	0.01000	
				20.5833	0.00775	0.01000	
				18.4247	0.00861	0.01000	

Sample Calculations

Run No. RD-2:

Reaction temperature $= 30^{\circ}C$

pH $= 11.0$

$$[S_2O_4^{--}] = 7.72 \times 10^{-5}\ M$$

$$[O_2] = 1.2 \times 10^{-3}\ M$$

This run has been plotted in Figure (3)

(a) Maximum Temperature Rise:

$$\Delta H_R \times M = \Delta T \times cp$$

$$\Delta T = 135.1 \times 7.72 \times 10^{-5}$$

$$= .0104^{\circ}C$$

(b) Reaction Rate:

$$\text{Slope} = 0.011585$$

$$\text{Reaction Rate} = \frac{\text{Slope}}{\Delta H_R} = \frac{0.011585}{135.1}$$

$$= 8.6 \times 10^{-5}\ M/sec$$

APPENDIX C

DATA FOR OXIDATION OF SODIUM DITHIONITE
INHIBITION WITH MANGANESE CHLORIDE

TABLE 12: RECORDED DATA FOR $MnCl_2$ INHIBITED O_2-SODIUM DITHIONITE SYSTEM

EFFECT OF MANGANESE CHLORIDE CONCENTRATION

Reaction Temperature = $30^{o}C$

pH = 8

Run No.	$MnCl_2$ added in Dithionite Solution (M)	$MnCl_2$ added in Oxygen solution (M)	Stock Solution: Concn. of Dithionite (M)	Stock Solution: Concn. of Oxygen (M)	Volume of the Reactor (cm^3)	Flow Rate of Dithionite Solution (ml/sec)	Flow Rate of Oxygen Solution (ml/sec)	Microvoltmeter output (mV)
1	2	3	4	5	6	7	8	9
RI-1	0.0001	0.0001	0.001	0.0013	0.16	1.5833	19.00	0.00344
					0.16	1.4247	17.10	0.00392
					0.16	1.2564	15.20	0.00446
					0.16	1.1875	14.25	0.00458
RI-2	0.0003	0.0003	0.001	0.0014	0.16	1.2564	15.20	0.00178
					0.16	1.1872	14.25	0.00197
					0.16	1.1081	13.30	0.00210
					0.16	0.9498	14.40	0.00242
					0.16	0.7916	9.50	0.00286
RI-3	0.0005	0.0005	0.001	0.0014	0.16	1.1872	14.25	0.00140
					0.16	0.9498	11.40	0.00181
					0.16	0.6332	7.60	0.00286

Table 12 (contd)

1	2	3	4	5	6	7	8	9
CI-4	0.0008	0.0008	0.001	0.0013	0.16	1.1872	14.25	0.00089
					0.16	0.7916	9.50	0.00134
					0.16	0.6332	7.60	0.00172
					0.16	0.4749	5.70	0.00223
					0116	0.3166	3.80	0.00331
CI-5	0.0010	0.0010	0.001	0.0013	0.16	0.9498	11.40	0.00083
					0.16	0.6332	7.60	0.00121
					0.16	0.4749	5.70	0.00166
					0.16	0.3166	3.80	0.00242
CI-6	0.0020	0.0020	0.001	0.0014	0.16	1.1081	13.30	0.00051
					0.16	0.7916	9.50	0.00070
					0.16	0.4749	5.70	0.00121
					0.16	0.3166	3.80	0.00178
					0.16	0.1583	1.90	0.00356
CI-7	0.0050	0.0050	0.001	0.0013	0.16	0.3166	3.80	0.00076
					2.53	1.5833	19.00	0.00229
					2.53	1.2564	15.20	0.00293
					2.53	0.9498	11.40	0.00382

Table 12 (contd)

1	2	3	4	5	6	7	8	9
CI-8	0.0080	0.0080	0.001	0.0014	0.16	0.3166	3.80	0.00051
					2.53	1.5833	19.00	0.00172
					2.53	1.2564	15.20	0.00210
					2.53	0.9498	11.40	0.00280
					2.53	0.7916	9.50	0.00337
					2.53	0.6332	7.60	0.00414
CI-9	0.0100	0.0100	0.001	0.0014	2.53	1.5833	19.00	0.00134
					2.53	1.2564	15.20	0.00172
					2.53	0.9498	11.40	0.00229
					5.02	1.4247	17.10	0.00312
					5.02	1.1081	13.30	0.00388
					2.53	0.4749	5.70	0.00452

TABLE 13: CALCULATED DATA FOR $MnCl_2$ INHIBITED O_2-SODIUM DITHIONITE SYSTEM

EFFECT OF $MnCl_2$ CONCENTRATION

Reaction Temperature=30°C

pH= 8

Run No.	In Reactor: Average $MnCl_2$ concn. (M)	In Reactor: Average Dithionite concn. (M)	In Reactor: Average Oxygen concn. (M)	Total Flow Rate (ml/sec)	Residence Time (sec)	Rise in Temperature (°C)	Reaction Rate (M/sec)
1	2	3	4	5	6	7	8
CI-1	0.0001	7.72×10^{-5}	0.0012	20.5833	0.00750	0.00540	5.285×10^{-3}
				18.4247	0.00861	0.00611	
				16.4564	0.00969	0.00700	
				15.4372	0.01033	0.00720	
CI-2	0.0003	7.72×10^{-5}	0.0013	16.4564	0.00969	0.00280	2.024×10^{-3}
				15.4372	0.01033	0.00310	
				14.4081	0.01107	0.00330	
				12.3498	0.01292	0.00380	
				10.2916	0.01550	0.00450	
CI-3	0.0005	7.72×10^{-5}	0.0013	15.4372	0.01033	0.00220	1.661×10^{-3}
				12.3498	0.01292	0.00285	
				8.2332	0.01937	0.00450	

Table 13 (contd)

1	2	3	4	5	6	7	8
CI-4	0.0008	7.72×10^{-5}	0.0012	15.4372	0.01033	0.00140	1.012×10^{-3}
				10.2916	0.01550	0.00210	
				8.2332	0.01937	0.00270	
				6.1749	0.02583	0.00351	
				4.1166	0.03875	0.00520	
CI-5	0.0010	7.72×10^{-5}	0.0012	12.3498	0.01292	0.00130	7.55×10^{-4}
				8.2332	0.01937	0.00190	
				6.1749	0.02583	0.00260	
				4.1166	0.03875	0.00380	
CI-6	0.0020	7.72×10^{-5}	0.0013	14.4081	0.01107	0.00080	5.322×10^{-4}
				10.2916	0.01550	0.00110	
				6.1749	0.02583	0.00190	
				4.1166	0.03875	0.00280	
				2.0583	0.07745	0.00560	
CI-7	0.0050	7.72×10^{-5}	0.0012	4.1166	0.03875	0.00120	2.270×10^{-4}
				20.5833	0.12292	0.00360	
				16.4664	0.15374	0.00460	
				12.3498	0.20486	0.00600	
				10.2916	0.24583	0.00700	

Table 13 (contd)

1	2	3	4	5	6	7	8
CI-8	0.0080	7.72×10^{-5}	0.0013	4.1166	0.03875	0.0008	1.600×10^{-4}
				20.5833	0.12292	0.0027	
				16.4664	0.15374	0.0033	
				12.3498	0.20486	0.0044	
				10.2916	0.24583	0.0053	
				8.2332	0.30729	0.0065	
CI-9	0.0100	7.72×10^{-5}	0.0013	20.5833	0.12292	0.0021	1.330×10^{-4}
				16.4664	0.15374	0.0027	
				12.3498	0.20486	0.0036	
				18.5247	0.27099	0.0049	
				14.4081	0.34842	0.0061	
				6.1749	0.40976	0.0071	

TABLE 14: RECORDED DATA FOR $MnCl_2$ INHIBITED O_2-SODIUM DITHIONITE SYSTEM

EFFECT OF OXYGEN CONCENTRATION

Reaction Temperature = 30^oC pH = 11

$MnCl_2$ added to Dithionite solution = $1.0x10^{-3}M$

$MnCl_2$ added to Oxygen solution = $1.0x10^{-3}M$

Run No.	Stock Solution: Concn of Dithionite Solution (M)	Stock Solution: Concn of Oxygen Solution (M)	Volume of the Reactor (cm^3)	Flow Rate of Dithionite Solution (ml/sec)	Flow Rate of Oxygen Solution (ml/sec)	Microvoltmeter output (mV)
1	2	3	4	5	6	7
OI-1	0.0010	0.00058	2.53	0.9498	11.40	0.00022
			2.53	0.4749	5.70	0.00045
			5.02	0.6332	7.60	0.00076
			14.43	1.1081	13.30	0.00108
			14.43	0.7916	9.50	0.00161
			14.43	0.4777	6.33	0.00236
OI-2	0.0010	0.00124	2.53	0.7916	9.50	0.00027
			5.02	0.7916	9.50	0.00052
			14.43	1.1081	13.30	0.00111
			14.43	0.6332	7.60	0.00197
			14.43	0.4749	5.70	0.00261

Table 14 (contd)

1	2	3	4	5	6	7
OI-3	0.0010	0.00239	2.53	0.9498	11.40	0.00022
			2.53	0.4749	5.70	0.00045
			14.43	1.5833	19.00	0.00080
			5.02	0.3166	3.80	0.00142
			14.43	0.4777	6.33	0.00236
OI-4	0.0010	0.00315	5.02	1.1872	14.25	0.00034
			14.43	1.4247	17.10	0.00090
			14.43	0.7916	9.50	0.00154
			14.43	0.6332	7.60	0.00194
			14.43	0.4749	5.70	0.00264

TABLE 15: CALCULATED DATA FOR $MnCl_2$ INHIBITED O_2-SODIUM DITHIONITE SYSTEM

EFFECT OF OXYGEN CONCENTRATION

Reaction Temperature = 30°C

Average $MnCl_2$ concentration in the Reactor = 1.0×10^{-3} M

Run No.	In Reactor: Average Dithionite Concn (M)	In Reactor: Average Oxygen Concn (M)	Total Flow Rate (ml/sec)	Residence Time (sec)	Temperature Rise (°C)	Reaction Rate (M/sec)
1	2	3	4	5	6	7
OI-1	7.72×10^{-5}	5.34×10^{-4}	12.3498	0.20486	0.00035	1.30×10^{-5}
			6.1749	0.40976	0.00071	
			8.2332	0.60973	0.00122	
			14.4081	1.00152	0.00170	
			10.2916	1.40211	0.00253	
			6.8107	2.11894	0.00370	
OI-2	7.72×10^{-5}	1.14×10^{-3}	10.2916	0.24583	0.00043	1.29×10^{-5}
			10.2916	0.48778	0.00082	
			14.4081	1.00152	0.00175	
			8.2332	1.75266	0.00311	
			6.1749	2.33688	0.00410	

Table 15 (contd)

1	2	3	4	5	6	7
OI-3	7.72×10^{-5}	2.22×10^{-3}	12.3498	0.20486	0.00035	1.31×10^{-5}
			6.1749	0.40976	0.00071	
			20.5833	0.70106	0.00125	
			4.1166	1.21945	0.00223	
			6.8107	2.11894	0.00374	
OI-4	7.72×10^{-5}	2.92×10^{-3}	15.4372	0.32519	0.00054	1.29×10^{-5}
			18.5247	0.77896	0.00141	
			10.2916	1.40211	0.00242	
			8.2332	1.75266	0.00305	
			6.1749	2.33688	0.00415	

TABLE 16: RECORDED DATA FOR $MnCl_2$ INHIBITED O_2-DITHIONITE SYSTEM

EFFECT OF DITHIONITE CONCENTRATION

Reaction Temperature = 30°C, pH = 11

$MnCl_2$ added in Dithionite Solution = 1.0×10^{-3} M

$MnCl_2$ added in Oxygen Solution = 1.0×10^{-3} M

Run No.	Stock Solution		Volume of the Reactor (cm^3)	Flow Rate of Dithionite Solution (ml/sec)	Flow Rate of Oxygen Solution (ml/sec)	Microvoltmeter output (mV)
	Concn of Dithionite Solution (M)	Concn of Oxygen Solution (M)				
1	2	3	4	5	6	7
DI-1	0.0005	0.0013	2.53	0.9498	11.40	0.00012
			2.53	0.4749	5.70	0.00023
			14.43	1.1081	13.30	0.00056
			14.43	0.7916	9.50	0.00078
			14.43	0.4777	6.33	0.00117
			14.43	0.3166	3.80	0.00194
DI-2	0.0010	0.00134	2.53	0.9498	11.40	0.00025
			2.53	0.4749	5.70	0.00051
			14.43	1.1081	13.30	0.00121
			14.43	0.7916	9.50	0.00175
			14.43	0.4777	6.33	0.00264

Table 16 (contd)

1	2	3	4	5	6	7
DI-3	0.0030	0.00141	2.53	0.9498	11.40	0.00064
			2.53	0.4749	5.70	0.00134
			14.43	1.1081	13.30	0.00344
			14.43	0.7916	9.50	0.00478
			14.43	0.4777	6.33	0.00726
			14.43	0.3166	3.80	0.01171
DI-4	0.0050	0.0013	2.53	0.9498	11.40	0.00102
			2.53	0.4749	5.70	0.00204
			14.43	1.1081	13.30	0.00509
			14.43	0.7916	9.50	0.00716
			14.43	0.4777	6.33	0.01069
			14.43	0.3166	3.80	0.01782
DI-5	0.0060	0.0015	2.53	0.9498	11.40	0.00115
			2.53	0.4749	5.70	0.00242
			14.43	1.1081	13.30	0.00598
			14.43	0.7916	9.50	0.00828
			14.43	0.4777	6.33	0.01248
			14.43	0.3166	3.80	0.02100

Table 16 (contd)

1	2	3	4	5	6	7
DI-6	0.0100	0.0014	2.53	0.9498	11.40	0.00223
			2.53	0.4749	5.70	0.00369
			14.43	1.1081	13.30	0.01114
			14.43	0.7916	9.50	0.01528
			14.43	0.4777	6.33	0.02355
			14.43	0.3166	3.80	0.03883
DI-7	0.0530	0.0013	2.53	0.9498	11.40	0.01209
			2.53	0.4749	5.70	0.02483
			5.02	0.7916	9.50	0.02992
			5.02	0.6332	7.60	0.03692
			5.02	0.4749	5.70	0.04902
			14.43	1.1081	13.30	0.06050
DI-8	0.1540	0.0013	0.16	0.1833	1.90	0.01337
			2.53	1.5833	19.00	0.02228
			2.53	0.9498	11.40	0.03629
			5.02	1.4247	17.10	0.04265
			5.02	1.1081	13.30	0.06302
			5.02	0.4749	5.70	0.07385

Table 16 (contd)

1	2	3	4	5	6	7
DI-9	0.5990	0.0014	0.16	1.1872	14.25	0.06366
			0.16	0.6332	7.60	0.01209
			0.16	0.3166	3.80	0.02610
			0.16	0.1833	1.90	0.05029
DI-10	1.3080	0.0013	0.16	1.4247	17.10	0.01400
			0.16	0.7916	9.50	0.02355
			0.16	0.4777	6.33	0.03565
			0.16	0.3166	3.80	0.05857

TABLE 17: CALCULATED DATA FOR $MnCl_2$ INHIBITED O_2-DITHIONITE SYSTEM

EFFECT OF DITHIONITE CONCENTRATION

Reaction temperature = $30^{o}C$, pH = 11

Average $MnCl_2$ concentration in the reactor = 1.0×10^{-3} M

Run No.	In Reactor: Average Dithionite conc. (M)	In Reactor: Average Oxygen conc. (M)	Total Flow Rate (ml/sec)	Residence Time (sec)	Rise in Temperature (°C)	Reaction Rate (M/sec)
1	2	3	4	5	6	7
DI-1	3.85×10^{-5}	0.0012	12.3498	0.20486	0.00018	6.40×10^{-6}
			6.1749	0.40976	0.00036	
			14.4081	1.00152	0.00088	
			10.2916	1.40211	0.00122	
			6.8107	2.11894	0.00184	
			4.1166	3.50532	0.00304	
DI-2	7.72×10^{-5}	0.0012	12.3498	0.20486	0.00040	1.29×10^{-5}
			6.1749	0.40976	0.00080	
			14.4081	1.00152	0.00190	
			10.2916	1.40211	0.00275	
			6.8107	2.11894	0.00415	
			4.1166	3.50532	0.00680	

Table 17 (contd)

1	2	3	4	5	6	7
DI-3	23.10×10^{-5}	0.0013	12.3498	0.20486	0.0010	4.06×10^{-5}
			6.1749	0.40976	0.0021	
			14.4081	1.00152	0.0054	
			10.2916	1.40211	0.0075	
			6.8107	2.11894	0.0114	
			4.1166	3.50532	0.0189	
DI-4	38.50×10^{-5}	0.0012	12.3498	0.20486	0.0016	6.34×10^{-5}
			6.1749	0.40976	0.0032	
			14.4081	1.00152	0.0080	
			10.2916	1.40211	0.0112	
			6.8107	2.11894	0.0168	
			4.1166	3.50532	0.0280	
DI-5	46.30×10^{-5}	0.0014	12.3498	0.20486	0.0018	6.87×10^{-5}
			6.1749	0.40976	0.0038	
			12.4081	1.00152	0.0094	
			10.2916	1.40211	0.0130	
			6.8107	2.11894	0.0196	
			4.1166	3.50532	0.0330	

Table 17 (contd)

1	2	3	4	5	6	7
DI-6	77.80×10^{-5}	0.0013	12.3498	0.20486	0.0035	1.28×10^{-4}
			6.1749	0.40976	0.0058	
			12.4081	1.00152	0.0175	
			10.2916	1.40211	0.0240	
			6.8107	2.11894	0.0270	
			4.1166	3.50532	0.0610	
DI-7	4.0×10^{-3}	0.0012	12.3498	0.20486	0.0190	7.02×10^{-4}
			6.1749	0.40976	0.0390	
			10.2916	0.48778	0.0470	
			8.2332	0.60973	0.0580	
			6.1749	0.81297	0.0770	
			14.4081	1.00152	0.0950	
DI-8	1.2×10^{-2}	0.0012	2.0583	0.07745	0.0210	21.06×10^{-4}
			20.5833	0.12292	0.0350	
			12.3498	0.20486	0.0570	
			18.5247	0.27099		
			14.4081	0. [illegible]		
			6.1749			

Table 17 (contd)

1	2	3	4	5	6	7
DI-9	4.6×10^{-2}	0.0013	15.4372	0.01033	0.0100	75.74×10^{-4}
			8.2332	0.01937	0.0190	
			4.1166	0.03875	0.0410	
			2.0583	0.07745	0.0790	
DI-10	1.0×10^{-1}	0.0012	18.4247	0.00861	0.0220	1.73×10^{-2}
			10.2916	0.01550	0.0570	
			6.8107	0.02342	0.0560	
			4.1166	0.03875	0.0920	

APPENDIX D

DATA FOR O_2-SODIUM DITHIONITE SYSTEM INHIBITION WITH MANGANESE SULFATE

TABLE 18: RECORDED DATA FOR $MnSO_4$ INHIBITED O_2-SODIUM DITHIONITE SYSTEM

EFFECT OF MANGANESE SULPHATE CONCENTRATION

Reaction temperature = $30^{o}C$, pH=8

Run No.	$MnSO_4$ added in Dithionite Solution (M)	$MnSO_4$ added in Oxygen Solution (M)	Stock Solution: Conc. of Dithionite (M)	Stock Solution: Conc. of Oxygen (M)	Volume of the Reactor (cm^3)	Flow Rate of Dithionite (ml/sec)	Flow rate of Oxygen (ml/sec)	Microvoltmeter output (mV)
1	2	3	4	5	6	7	8	9
SI-1	0.0001	0.0001	0.001	0.0014	0.16	1.5833	19.00	0.00331
					0.16	1.4247	17.10	0.00369
					0.16	1.2564	15.20	0.00427
					0.16	1.1872	14.25	0.00439
SI-2	0.0003	0.0003	0.001	0.0013	0.16	1.2564	15.20	0.00153
					0.16	1.1872	14.25	0.00159
					0.16	1.1081	13.30	0.00179
					0.16	0.9498	11.40	0.00204
					0.16	0.7916	9.50	0.00236
SI-3	0.0008	0.0008	0.001	0.0014	0.16	1.1872	14.25	0.00076
					0.16	0.7916	9.50	0.00115
					0.16	0.6332	7.60	0.00146
					0.16	0.4749	5.70	0.00197

Table 18 (contd)

1	2	3	4	5	6	7	8	9
SI-4	0.001	0.001	0.001	0.0014	0.16	0.9498	11.40	0.00070
					0.16	0.6332	7.60	0.00108
					0.16	0.4749	5.70	0.00146
					0.16	0.3166	3.80	0.00223
SI-5	0.002	0.002	0.001	0.0013	0.16	1.1081	13.30	0.00048
					0.16	0.7916	9.50	0.00057
					0.16	0.4749	5.70	0.00102
					0.16	0.3166	3.80	0.00146
					0.16	0.1583	1.90	0.00299
SI-6	0.005	0.005	0.001	0.0015	0.16	0.3166	3.80	0.00051
					2.53	1.5833	19.00	0.00172
					2.53	1.2564	15.20	0.00223
					2.53	0.9498	11.40	0.00285
					2.53	0.7916	9.50	0.00363
SI-7	0.008	0.008	0.001	0.0013	0.16	0.3166	3.80	0.00038
					2.53	1.5833	19.00	0.00115
					2.53	1.2564	15.20	0.00146
					2.53	0.9498	11.40	0.00185

Table 18 (contd)

1	2	3	4	5	6	7	8	9
					2.53	0.7916	9.50	0.00236
					2.53	0.6332	7.60	0.00286
SI-8	0.01	0.01	0.001	0.0014	2.53	1.5833	19.00	0.00095
					2.53	1.2564	15.20	0.00115
					2.53	0.9498	11.40	0.00153
					5.02	1.4247	17.10	0.00216
					5.02	1.1081	13.30	0.00267
					2.53	0.4749	5.70	0.00306

TABLE 19: CALCULATED DATA FOR $MnSO_4$ INHIBITED O_2 - SODIUM DITHIONITE SYSTEM

EFFECT OF $MnSO_4$ CONCENTRATION

Reaction temperature = $30^\circ C$; pH=8

Run No.	In Reactor: Average $MnSO_4$ conc. (M)	In Reactor: Average Dithionite conc. (M)	In Reactor: Average Oxygen conc. (M)	Total Flow Rate (ml/sec)	Residence Time (sec)	Temperature Rise ($^\circ C$)	Reaction Rate (M/sec)
1	2	3	4	5	6	7	8
SI-1	0.0001	7.72×10^{-5}	0.0013	20.5833	0.00755	0.0052	51.20×10^{-4}
				18.4247	0.00861	0.0058	
				16.4564	0.00969	0.0067	
				15.4372	0.01033	0.0069	
SI-2	0.0003	7.72×10^{-5}	0.0012	16.4564	0.00969	0.0024	18.60×10^{-4}
				15.4372	0.01033	0.0025	
				14.4081	0.01107	0.0028	
				12.3498	0.01292	0.0032	
				10.2916	0.01550	0.0037	
SI-3	0.0008	7.72×10^{-5}	0.0013	15.4375	0.01033	0.0012	8.70×10^{-4}
				10.2916	0.01550	0.0018	
				8.2332	0.01937	0.0023	
				6.1749	0.02583	0.0031	

Table 19 (contd)

1	2	3	4	5	6	7	8
SI-4	0.001	7.72×10^{-5}	0.0013	12.3498	0.01292	0.0011	6.82×10^{-4}
				8.2332	0.01937	0.0017	
				6.1749	0.02583	0.0023	
				4.1166	0.03875	0.0035	
SI-5	0.002	7.72×10^{-5}	0.0012	14.4081	0.01107	0.0006	4.42×10^{-4}
				10.2916	0.01550	0.0009	
				6.1749	0.02583	0.0016	
				4.1166	0.03875	0.0023	
				2.0583	0.07745	0.0047	
SI-6	0.005	7.72×10^{-5}	0.0014	4.1166	0.03875	0.0008	1.68×10^{-4}
				20.5833	0.12292	0.0027	
				16.4664	0.15374	0.0035	
				12.3498	0.20486	0.0045	
				10.2916	0.24583	0.0057	
SI-7	0.008	7.72×10^{-5}	0.0012	4.1166	0.03875	0.0006	1.12×10^{-4}
				20.5833	0.12292	0.0018	
				16.4664	0.15374	0.0023	
				12.3498	0.20486	0.0029	

Table 19 (contd)

1	2	3	4	5	6	7	8
				8.2332	0.30729	0.0045	
SI-8	0.01	7.72×10^{-5}	0.0013	20.5833	0.12292	0.0015	0.89×10^{-4}
				16.4664	0.15374	0.0018	
				12.3498	0.20486	0.0024	
				18.5247	0.27099	0.0034	
				14.4081	0.34842	0.0042	
				6.1749	0.40976	0.0048	

TABLE 20: RECORDED DATA FOR $MnSO_4$ INHIBITED O_2-SODIUM DITHIONITE SYSTEM

EFFECT OF OXYGEN CONCENTRATION

Reaction temperature = $30^{\circ}C$, pH=11

$MnSO_4$ added to the Dithionite Solution = 1.0×10^{-3}M

$MnSO_4$ added to the Oxygen Solution = 1.0×10^{-3}M

Run No.	Stock Solution: Conc. of Dithionite Solution (M)	Stock Solution: Conc. of Oxygen Solution (M)	Volume of the Reactor (cm^3)	Flow Rate of Dithionite Solution (ml/sec)	Flow Rate of Oxygen Solution (ml/sec)	Microvoltmeter Output (mV)
1	2	3	4	5	6	7
OS-1	0.001	0.0006	2.53	0.9498	11.40	0.00013
			2.53	0.4749	5.70	0.00032
			5.02	0.6332	7.60	0.00051
			14.43	1.1081	13.30	0.00089
			14.43	0.7916	9.50	0.00115
			14.43	0.4777	6.33	0.00178
OS-2	0.001	0.0013	2.53	0.9498	11.40	0.00019
			5.02	0.7916	9.50	0.00051
			14.43	1.1081	13.30	0.00095
			14.43	0.6332	7.60	0.00166
			14.43	0.4749	5.70	0.00223

Table 20 (contd)

1	2	3	4	5	6	7
OS-3	0.001	0.0024	2.53	0.9498	11.40	0.00025
			2.53	0.4749	5.70	0.00045
			14.43	1.5833	19.00	0.00070
			5.02	0.3166	3.80	0.00121
			14.43	0.4777	6.33	0.00216
OS-4	0.001	0.003	5.02	1.1872	14.25	0.00032
			14.43	1.4247	17.10	0.00070
			14.43	0.7916	9.50	0.00127
			14.43	0.6332	7.60	0.00159
			14.43	0.4749	5.70	0.00216

TABLE 21: CALCULATED DATA FOR $MnSO_4$ INHIBITED O_2-SODIUM DITHIONITE SYSTEM

EFFECT OF OXYGEN CONCENTRATION

Reaction temperature = $30^{o}C$, pH = 11

Average $MnSO_4$ Concentration in the reactor = 1.0×10^{-3}M

Run No.	In Reactor: Average Dithionite conc. (M)	In Reactor: Average Oxygen conc. (M)	Total Flow Rate (ml/sec)	Residence Time (sec)	Rise in Temperature (^{o}C)	Reaction Rate (M/sec)
1	2	3	4	5	6	7
OS-1	7.72×10^{-5}	5.55×10^{-4}	12.3498	0.20486	0.0002	1.00×10^{-5}
			6.1749	0.40976	0.0005	
			8.2332	0.60973	0.0008	
			14.4081	1.00152	0.0014	
			10.2916	1.40211	0.0018	
			6.8107	2.11894	0.0028	
OS-2	7.72×10^{-5}	0.0012	12.3498	0.20486	0.0003	1.10×10^{-5}
			10.2916	0.48778	0.0008	
			14.4081	1.00152	0.0015	
			8.2332	1.75266	0.0026	
			6.1749	2.33688	0.0035	

Table 21 (contd)

1	2	3	4	5	6	7
OS-3	7.72×10^{-5}	2.22×10^{-3}	12.3498	0.20486	0.0004	1.20×10^{-5}
			6.1749	0.40976	0.0007	
			20.5833	0.70166	0.0011	
			4.1166	1.21945	0.0019	
			6.8107	2.11894	0.0034	
OS-4	7.72×10^{-5}	2.76×10^{-3}	15.4372	0.32519	0.0005	1.08×10^{-5}
			18.5247	0.77896	0.0011	
			10.2916	1.40211	0.0020	
			8.2532	1.75266	0.0025	
			6.1749	2.33688	0.0034	

TABLE 22: RECORDED DATA FOR $MnSO_4$ INHIBITED O_2-SODIUM DITHIONITE SYSTEM

EFFECT OF SODIUM DITHIONITE CONCENTRATION

Reaction temperature = $30^{o}C$, pH = 11

$MnSO_4$ added to the Dithionite Solution = $1.0\times10^{-3}M$

$MnSO_4$ added to the Oxygen Solution = $1.0 \times 10^{-3}M$

Run No.	Stock Solution: Conc. of Dithionite (M)	Stock Solution: Conc. of Oxygen (M)	Volume of the Reactor (cm^3)	Flow Rate of Dithionite Solution (ml/sec)	Flow Rate of Oxygen Solution (ml/sec)	Microvoltmeter Output (mV)
1	2	3	4	5	6	7
DS-1	0.0005	0.0013	2.53	0.9498	11.40	0.00006
			2.53	0.4749	5.70	0.00019
			14.43	1.1081	13.30	0.00045
			14.43	0.7916	9.50	0.00057
			14.43	0.4777	6.33	0.00089
			14.43	0.3166	3.80	0.00153
DS-2	0.0010	0.0014	2.53	0.9498	11.40	0.00019
			2.53	0.4749	5.70	0.00038
			14.43	1.1081	13.30	0.00089
			14.43	0.7916	9.50	0.00134
			14.43	0.4777	6.33	0.00204
			14.43	0.3166	3.80	0.00331

Table 22 (contd)

1	2	3	3	4	5	6	7
DS-3	0.003		0.0013	2.53	0.9498	11.40	0.00064
				2.53	0.4749	5.70	0.00115
				14.43	0.1081	13.30	0.00306
				14.43	0.7916	9.50	0.00427
				14.43	0.4777	6.33	0.00662
				14.43	0.3166	3.80	0.00929
DS-4	0.0010		0.0015	2.53	0.9498	11.40	0.00127
				2.53	0.4749	5.70	0.00382
				14.43	0.1081	13.30	0.01019
				14.43	0.7916	9.50	0.01401
				14.43	0.4777	6.33	0.02164
				14.43	0.3166	3.80	0.03565
DS-5	0.0053		0.0013	2.53	0.9498	11.40	0.00955
				2.53	0.4749	5.70	0.01937
				5.02	0.7916	9.50	0.02355
				5.02	0.6332	7.60	0.02928
				5.02	0.4749	5.70	0.03883
				14.43	1.1081	13.30	0.04711

Table 22 (contd)

1	2	3	4	5	6	7
DS-6	0.152	0.0013	0.16	0.1583	1.90	0.10820
			2.53	1.5833	19.00	0.01719
			2.53	0.9498	11.40	0.02737
			5.02	1.4247	17.10	0.03756
			5.02	1.1081	13.30	0.04711
			2.53	0.4749	5.70	0.05602

TABLE 23: CALCULATED DATA FOR $MnSO_4$ INHIBITED O_2-SODIUM DITHIONITE SYSTEM

EFFECT OF SODIUM DITHIONITE CONCENTRATION

Reaction temperature = $30^{\circ}C$; pH = 11

Average $MnSO_4$ concentration in the reactor = 1.0×10^{-3}M

Run No.	In Reactor: Average Dithionite conc. (M)	In Reactor: Average Oxygen conc. (M)	Total Flow Rate (ml/sec)	Residence Time (sec)	Rise in Temperature ($^{\circ}C$)	Reaction Rate (M/sec)
1	2	3	4	5	6	7
DS-1	3.85×10^{-5}	0.0012	12.3498	0.20486	0.0001	5.0×10^{-6}
			6.1749	0.40976	0.0003	
			14.4081	1.00152	0.0007	
			10.2916	1.40211	0.0009	
			6.8107	2.11894	0.0014	
			4.1166	3.50532	0.0024	
DS-2	7.72×10^{-5}	0.0013	12.3498	0.20486	0.0003	1.1×10^{-5}
			6.1749	0.40976	0.0006	
			14.4081	1.00152	0.0014	
			10.2916	1.40211	0.0021	
			6.8107	2.11894	0.0032	
			4.1166	3.50532	0.0052	

Table 23 (contd)

1	2	3	4	5	6	7
DS-3	23.1×10^{-5}	0.0012	12.3498	0.20486	0.0010	3.6×10^{-5}
			6.1749	0.40976	0.0018	
			14.4081	1.00152	0.0048	
			10.2916	1.40211	0.0067	
			6.8107	2.11894	0.0104	
			4.1166	3.50532	0.0146	
DS-4	77.8×10^{-5}	0.0014	12.3498	0.20486	0.0020	10.8×10^{-5}
			6.1749	0.40976	0.0060	
			14.4081	1.00152	0.0160	
			10.2916	1.40211	0.0220	
			6.8107	2.11894	0.0340	
			4.1166	3.50532	0.0560	
DS-5	4.1×10^{-3}	0.0012	12.3498	0.20486	0.0150	55.2×10^{-5}
			4.1179	0.40976	0.0310	
			10.2916	0.48778	0.0370	
			8.2332	0.60973	0.0460	
			6.1749	0.81297	0.0610	

Table 23 (contd)

1	2	3	4	5	6	7
DS-6	1.16×10^{-2}	0.0012	2.0583	0.07745	0.017	16.1×10^{-4}
			20.5833	0.12292	0.027	
			12.3498	0.20486	0.043	
			18.5247	0.27099	0.059	
			14.4081	0.34842	0.074	
			6.1749	0.40972	0.088	

APPENDIX E

DATA FOR O_2-SODIUM DITHIONITE SYSTEM - INHIBITION WITH TRIETHANOLAMINE

TABLE 24: RECORDED DATA FOR TRIETHANOLAMINE INHIBITED O_2-SODIUM DITHIONITE SYSTEM

EFFECT OF TRIETHANOLAMINE CONCENTRATION

Reaction temperature = 30°C ; pH = 8

Run No.	$(OHCH_2CH_2)_3N$ added in Dithionite Solution (M)	$(OHCH_2CH_2)_3N$ added in Oxygen Solution (M)	Stock Solution: Conc. of Dithionite (M)	Stock Solution: Conc. of Oxygen (M)	Volume of the Reactor (cm^3)	Flow Rate of Dithionite Solution (ml/sec)	Flow Rate of Oxygen Solution (ml/sec)	Microvoltmeter Output (mV)
1	2	3	4	5	6	7	8	9
TI-1	0.0001	0.0001	0.001	0.0014	0.16	2.3745	28.50	0.00197
					0.16	1.8996	22.80	0.00242
					0.16	1.5833	19.00	0.00286
					0.16	1.2564	15.20	0.00356
					0.16	1.1872	14.25	0.00376
TI-2	0.0003	0.0003	0.001	0.0016	0.16	2.3745	28.50	0.00140
					0.16	1.5833	19.00	0.00210
					0.16	1.4247	17.10	0.00242
					0.16	1.1872	14.25	0.00274
					0.16	1.1081	13.30	0.00306
					0.16	0.9498	11.40	0.00350

Table 24 (contd)

1	2	3	4	5	6	7	8	9
TI-3	0.0008	0.0008	0.001	0.0015	0.16	2.3745	22.80	0.00140
					0.16	1.5833	19.00	0.00204
					0.16	1.4247	17.10	0.00229
					0.16	1.1081	13.30	0.00293
					0.16	0.7916	9.50	0.00407
TI-4	0.0010	0.0010	0.001	0.0013	0.16	2.3745	22.80	0.00115
					0.16	1.4247	17.10	0.00185
					0.16	1.1081	13.30	0.00248
					0.16	0.7916	9.50	0.00325
					0.16	0.6332	7.60	0.00427
TI-5	0.0020	0.0020	0.001	0.0014	0.16	2.3745	22.80	0.00108
					0.16	1.4247	17.10	0.00178
					0.16	1.1872	14.25	0.00210
					0.16	0.7916	9.50	0.00312
					0.16	0.6332	7.60	0.00407
TI-6	0.0050	0.0050	0.001	0.0013	0.16	2.3745	22.80	[illegible]
					0.16	1.5833		
					0.16	[illegible]		

Table 24 (contd)

1	2	3	4	5	6	7	8	9
					0.16	0.6332	7.60	0.00344
					0.16	0.4777	6.33	0.00401
TI-7	0.008	0.008	0.001	0.0015	0.16	2.3745	28.50	0.00089
					0.16	1.5833	19.00	0.00121
					0.16	1.1872	14.25	0.00159
					0.16	0.6332	7.60	0.00318
					0.16	0.4777	6.33	0.00363
TI-8	0.010	0.010	0.001	0.0015	0.16	1.5833	19.00	0.00083
					0.16	1.1872	14.25	0.00153
					0.16	0.6332	7.60	0.00306
					0.16	0.4749	5.70	0.00401

TABLE 25: CALCULATED DATA FOR TRIETHANOLAMINE INHIBITED O_2-SODIUM DITHIONITE SYSTEM

EFFECT OF TRIETHANOLAMINE CONCENTRATION

Reaction temperature = 30°C, pH=8

Run No.	In Reactor: Average Triethanol-amine conc. (M)	In Reactor: Average Dithionite conc. (M)	In Reactor: Average Oxygen conc. (M)	Total Flow Rate (ml/sec)	Residence Time (sec)	Rise in Temperature (°C)	Reaction Rate (M/sec)
1	2	3	4	5	6	7	8
TI-1	0.0001	7.72×10^{-5}	0.0013	30.8745	0.00517	0.0031	4.3×10^{-3}
				24.6996	0.00646	0.0038	
				20.5833	0.00775	0.0045	
				16.4564	0.00969	0.0056	
				15.4372	0.01033	0.0059	
TI-2	0.0003	7.72×10^{-5}	0.0015	30.8745	0.00517	0.0022	3.2×10^{-3}
				20.5833	0.00775	0.0033	
				18.4247	0.00861	0.0038	
				15.4372	0.01033	0.0043	
				14.4081	0.01107	0.0048	
				12.3498	0.01292	0.0055	
TI-3	0.0008	7.72×10^{-5}	0.0014	30.8745	0.00517	0.0022	3.1×10^{-3}
				20.5833	0.00775	0.0032	

Table 25 (contd)

1	2	3	4	5	6	7	8
				18.4247	0.00861	0.0036	
				15.4372	0.01033	0.0042	
				14.4081	0.01107	0.0046	
				10.2916	0.01550	0.0064	
TI-4	0.001	7.72×10^{-5}	0.0012	30.8745	0.00517	0.0018	2.5×10^{-3}
				18.4247	0.00861	0.0029	
				14.4081	0.01107	0.0039	
				10.2916	0.01550	0.0051	
				8.2332	0.01937	0.0067	
TI-5	0.002	7.72×10^{-5}	0.0013	30.8745	0.00517	0.0017	2.4×10^{-3}
				18.4247	0.00861	0.0028	
				15.4372	0.01033	0.0033	
				10.2916	0.01550	0.0049	
				8.2332	0.01937	0.0064	
TI-6	0.005	7.72×10^{-5}	0.0012	30.8745	0.00517	0.0019	2.0×10^{-3}
				20.5833	0.00775	0.0021	
				15.4372	0.01033	0.0027	
				8.2332	0.01937	0.0051	

Table 25 (contd)

1	2	3	4	5	6	7	8
				6.8107	0.02342	0.0063	
TI-7	0.008	7.72×10^{-5}	0.0014	30.8745	0.00517	0.0014	1.85×10^{-3}
				20.5833	0.00775	0.0019	
				15.4372	0.01033	0.0025	
				8.2332	0.01937	0.0050	
				6.8107	0.02342	0.0057	
TI-8	0.010	7.72×10^{-5}	0.0014	20.5833	0.00775	0.0013	1.79×10^{-3}
				15.4372	0.01033	0.0024	
				8.2332	0.01937	0.0048	
				6.1749	0.02583	0.0063	

TABLE 26: RECORDED DATA FOR TRIETHANOLAMINE INHIBITED O_2-SODIUM DITHIONITE SYSTEM

EFFECT OF OXYGEN CONCENTRATION

Reaction temperature = $30^{o}C$; pH = 11

Triethanolamine added to Dithionite Solution = $1.0x10^{-3}M$

Triethanolamine added to Oxygen Solution = $1.0x10^{-3}M$

Run No.	Stock Solution: Conc. of Dithionite Solution (M)	Stock Solution: Conc. of Oxygen Solution (M)	Volume of Reactor (cm^3)	Flow Rate of Dithionite Solution (ml/sec)	Flow Rate of Oxygen Solution (ml/sec)	Microvoltmeter Output (mV)
1	2	3	4	5	6	7
OT-1	0.001	0.0006	2.53	0.5498	11.40	0.00076
			2.53	0.4749	5.70	0.00146
			5.02	0.6332	7.60	0.00229
			5.02	0.4749	5.70	0.00293
			14.43	1.1081	13.30	0.00363
OT-2	0.001	0.0015	2.53	1.1081	13.30	0.00064
			5.02	1.4247	17.10	0.00108
			2.53	0.4777	6.33	0.00127
			5.02	0.6332	7.60	0.00229
			14.43	1.4247	17.10	0.00255
			14.43	1.1081	13.30	0.00363

Table 26 (contd)

1	2	3	4	5	6	7
OT-3	0.001	0.0021	2.53	0.9498	11.40	0.00076
			2.53	0.4749	5.70	0.00153
			5.02	0.6332	7.60	0.00223
			5.02	0.4749	5.70	0.00293
			14.43	1.1081	13.30	0.00363
OT-4	0.001	0.0030	2.53	1.1081	13.30	0.00076
			5.02	1.4247	17.10	0.00102
			5.02	1.1081	13.30	0.00127
			5.02	0.6332	7.60	0.00229
			14.43	1.2564	15.20	0.00325

TABLE 27: CALCULATED DATA FOR TRIETHANOLAMINE INHIBITED O_2-SODIUM DITHIONITE SYSTEM

EFFECT OF OXYGEN CONCENTRATION

Reaction temperature = 30°C; pH=11

Triethanolamine added to the Reactor = 1.0×10^{-3}M

Run No.	In Reactor: Average Dithionite conc. (M)	In Reactor: Average Oxygen conc. (M)	Total Flow Rate (ml/sec)	Residence Time (sec)	Rise in Temperature (°C)	Reaction Rate (M/sec)
1	2	3	4	5	6	7
OT-1	7.72×10^{-5}	5.5×10^{-4}	12.3498	0.20486	0.0012	4.24×10^{-5}
			6.1749	0.40976	0.0023	
			8.2332	0.60973	0.0036	
			6.1749	0.81297	0.0046	
			14.4081	1.00152	0.0057	
OT-2	7.72×10^{-5}	1.39×10^{-3}	14.4081	0.17560	0.0010	4.24×10^{-5}
			18.5247	0.27099	0.0017	
			6.8107	0.37151	0.0020	
			8.2332	0.60973	0.0036	
			18.5247	0.77896	0.0040	
			14.4081	1.00152	0.0057	

Table 27 (contd)

1	2	3	4	5	6	7
OT-3	7.72×10^{-5}	1.94×10^{-3}	12.3498	0.20486	0.0012	4.20×10^{-5}
			6.1749	0.40976	0.0024	
			8.2332	0.60973	0.0035	
			6.1749	0.81297	0.0046	
			14.4081	1.00152	0.0057	
OT-4	7.72×10^{-5}	2.78×10^{-3}	14.4081	0.17560	0.0012	4.26×10^{-5}
			18.5247	0.27099	0.0016	
			14.4081	0.34842	0.0020	
			8.2332	0.60973	0.0036	
			16.4564	0.87687	0.0051	

Table 28 (contd)

1	2	3	4	5	6	7
DT-3	0.003	0.0013	2.53	0.9498	11.40	0.00166
			2.53	0.4749	5.70	0.00331
			5.02	0.6332	7.60	0.00509
			5.02	0.4749	5.70	0.00675
			14.43	1.1081	13.30	0.00828
			5.02	0.3166	3.80	0.01019
			14.43	0.7916	9.50	0.01171
DT-4	0.010	0.0014	2.53	0.9498	11.40	0.00573
			2.53	0.4749	5.70	0.01178
			5.02	0.6332	7.60	0.01751
			5.02	0.4747	5.70	0.02260
			14.43	1.1081	13.30	0.02928
			5.02	0.3166	3.80	0.03374
			14.43	0.7916	9.50	0.03947
DT-5	0.052	0.0015	0.16	0.1583	1.90	0.01528
			2.53	1.4247	17.10	0.02801
			2.53	1.1081	13.30	0.03501
			2.53	0.9498	11.4[illegible]	0.04011

Table 28 (contd)

1	2	3	4	5	6	7
			5.02	1.4247	17.10	0.05411
DT-6	0.153	0.0015	0.16	0.7916	9.50	0.00955
			0.16	0.3166	3.80	0.02419
			0.16	0.1583	1.90	0.04520
			2.53	1.5833	19.00	0.07251
			2.53	1.4247	17.10	0.07958

TABLE 29: CALCULATED DATA FOR TRIETHANOLAMINE INHIBITED O_2-SODIUM DITHIONITE SYSTEM

EFFECT OF DITHIONITE CONCENTRATION

Reaction temperature = 30 ^{o}C ; pH = 11

Average triethanolamine added to the reactor = 1.0 $\times 10^{-3}$ M

Run No.	In Reactor: Average Dithionite conc. (M)	In Reactor: Average Oxygen conc. (M)	Total Flow Rate (ml/sec)	Residence Time (sec)	Rise in Temperature (^{o}C)	Reaction Rate (M/sec)
1	2	3	4	5	6	7
DT-1	3.85×10^{-5}	0.0015	2.0583	0.07745	0.0003	2.45×10^{-5}
			6.1749	0.40976	0.0013	
			8.2332	0.60973	0.0020	
			20.5833	0.70106	0.0023	
			6.1749	0.81297	0.0027	
			14.4081	1.00152	0.0033	
DT-2	7.72×10^{-5}	0.0013	2.0583	0.07745	0.0005	4.28×10^{-5}
			6.1749	0.40976	0.0024	
			8.2332	0.60973	0.0036	
			20.5833	0.70106	0.0041	
			6.1749	0.81297	0.0047	
			14.4081	1.00152	0.0058	

Table 29 (contd)

1	2	3	4	5	6	7
DT-3	23.1×10^{-5}	0.0012	12.3498	0.20486	0.0026	1.29×10^{-4}
			6. 1749	0.40976	0.0052	
			8.2332	0.60973	0.0080	
			6.1749	0.81297	0.0106	
			14.4081	1.00152	0.0130	
			4.1166	1.21945	0.0160	
			10.2916	1.40211	0.0184	
DT-4	77.0×10^{-5}	0.0013	12.3498	1.20486	0.0090	3.32×10^{-4}
			6.1749	0.40976	0.0185	
			8.2332	0.60973	0.0275	
			6.1749	0.81297	0.0355	
			14.4081	1.00152	0.0460	
			4.1166	1.21945	0.0530	
			10.2916	1.40211	0.0620	
DT-5	4.08×10^{-3}	0.0014	2.0583	0.07745	0.0240	2.69×10^{-3}
			18.5247	0.13665	0.0440	
			14.4081	0.17560	0.0550	

Table 29 (contd)

1	2	3	4	5	6	7
			12.3498	0.20486	0.0630	
			18.5247	0.27099	0.0850	
DT-6	1.16×10^{-2}	0.0014	10.2916	0.01550	0.0150	6.87×10^{-3}
			4.1166	0.03875	0.0380	
			2.0583	0.07745	0.0710	
			20.5833	0.12292	0.1140	
			18.5247	0.13665	0.1250	